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Raman Effect, Infra-Red Absorption, Dielectric Constant, and Electron Diffraction in Relation to Internal Rotation

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The relative intensities of Raman lines of 1,2-dichloroethane were determined in the gaseous state as well as in the liquid state. The result combined with that of the dipole measurement in the gaseous state enabled us to determine the equilibrium isomeric ratio of the *trans*- and the gauche molecules, which was in good agreement with that obtained from the absorption measurement of infra-red spectra. This ratio could also explain satisfactorily the result of an electron diffraction experiment made by us for the vapor of 1,2-dichloroethane. The statistical entropy of dihalogenoethanes was calculated from the molecular data and was compared with the third law entropy obtained from the thermal measurement. The frequencies of torsional oscillation about the C−C bond as axis were determined by the difference method and were found to be in agreement with the lowest frequencies of the observed Raman spectra.

IN the present note we report our researches on internal rotation of molecules of dihalogenoethanes made as the continuation of our previous works[1] which were published in this journal and in others until December 1941.

RAMAN EFFECT

In our previous papers we reported the Raman spectra of dihalogenoethanes XH_2C-CH_2X observed in the liquid and solid states. From this experimental result combined with the calculation of normal frequencies[2] and the consideration of selection rules it was concluded that in the solid state all the molecules assume the *trans*-form in which the two halogen atoms are at the farthest distance apart (Fig. 1). Therefore the internal rotation about the C−C bond as axis must be frozen in the solid state, which is due to the crystal forces. In addition to the Raman lines of the solid there were observed many other lines in the liquid state and in solutions (Table I), from which we have to consider the coexistence of at least one other molecular configuration in these states of aggregation. That the latter configuration corresponds to the gauche form (i.e. a form which can be obtained from the trans form by an internal rotation of about 120°) can be seen from the Raman spectrum of the molecule of the type X_3C-CH_2X, which according to this view gives only one form, and therefore, shows no change of Raman spectrum on solidification. It can therefore be concluded that for the molecule of dihalogenoethane there are three potential minima in one complete rotation about the C−C bond as axis, one of them corresponding to the trans form and the other two to the gauche forms. (Each of these two gauche forms is the mirror image of the other.)

To these previous results we supplemented the spectrum of 1,2-dichloroethane in the gaseous state, for which we observed the Raman lines as shown in Table I.[3] With slight modification in frequency all the important Raman lines of the liquid were observed in the gaseous state, from which we can show the coexistence of the trans and the gauche forms in the gaseous state also in conformity with the experimental results described below. The intensity relations of the lines are, however, different in these two states of aggregation: e.g. the intensity ratio $I(768)/I(666)$ of the two lines 768 cm^{-1} (of the *trans*-form) and 666 cm^{-1} (of the gauche form) amounts to

[1] Our previous works are summarized in Mizushima and Morino, Bull. Chem. Soc. Japan **17**, 94 (1942). See also Mizushima, Morino, and Takeda, J. Chem. Phys. **9**, 826 (1941).

[2] Mizushima, Morino, and Simanouti, Sci. Papers Inst. Phys. Chem. Research (Tokyo) **40**, 87 (1942).

[3] Morino, Watanabe, and Mizushima, *ibid.* **39**, 396 (1942).

TABLE I. 1,2-Dichloroethane.

Raman effect			Infra-red absorption*	
Gas	Liquid	Solid	Gas	Liquid
		66 (4*b*)		
	125 (5b)			
	223 (00)			
	265 (5)			
301 (7)	300 (8)	302 (5)		
	411 (5)			
666 (4)	654 (8)			
689 (0)	677 (6*b*)			
	(709) (0)		720 (st)	710 (st)
768 (10)	754 (10*b*)	750 (10)		
			770 (w)	770 (w)
	881 (4)		888 (med)	880 (st)
950 (0) ?	943 (5)		942 (w)	941 (st)
	989 (2)	992 (3)		
	1031 (2)		1034 (w)	1030 (med)
1040 (0) ?	1052 (4)	1059 (3)		
	1145 (3)			1144 (w)
	1207 (5)			
			1236 (b. st)	1236 (st)
	1264 (3)	1265 (2*b*)		
			1297 (med)	1297 (st)
1305 (3)	1304 (6)	1301 (5*b*)		
	1393 (1)			
	1429 (6)			
	1445 (4*b*)	1448 (2*b*)	1456 (st)	1425 (st)
	2844 (3)			
2887 (1) ?	2874 (4)	2874 (3)		
2962 (8)	2957 (10)	2964 (10)		
2978 (8)				
	3005 (8*b*)	3005 (6)		

* The infra-red absorption was measured in the frequency region between 700 and 1500 cm^{-1}.

5:1 at 170°C in the gaseous state, while it amounts to 2.0:1 at 150°C and to 1.8:1 at 25°C in the liquid state. This means that the energy difference between the *trans*- and the gauche molecules changes considerably by the change of states of aggregation.*

DIELECTRIC CONSTANT

In addition to the dipole measurement in solutions reported in our previous papers the dielectric constant of 1,2-dichloroethane was measured in the gaseous state,[4] the result of which was in good agreement with that of Zahn's[5] measurement. From this experimental result the equilibrium ratio of the trans and the gauche forms was determined as follows. Let N_t and m_t be the number and dipole moment of the trans molecules and N_g and m_g be the corresponding quantities of the gauche molecules. Then the mean moment is calculated as

$$m^2=(m_t^2N_t+m_g^2N_g/N_t+N_g). \quad (1)$$

In equilibrium we have

$$N_g/N_t=2(f_g/f_t)e^{-(\Delta E/kT)} \quad (2)$$

where ΔE is the energy difference between the trans and the gauche troughs; f_t and f_g are the partition functions of the trans and the gauche molecules,[6] and the factor 2 is introduced to account for the optical isomerism of the gauche form.

The value of m at different temperatures being known from our measurement, we can calculate ΔE and m_g from Eqs. (1) and (2):**

$$\Delta E=1.21 \text{ kcal/mole}$$
$$m_g=2.55\times10^{-18} \text{ e.s.u.} \quad (3)$$

From this value of ΔE and those of partition functions we can calculate the equilibrium ratio of the *trans*- and the gauche molecules at any temperature: e.g. we have for the vapor of 1,2-dichloroethane at its boiling point

$$N_g:N_t=0.34:1.$$

The equilibrium ratio in the liquid state cannot be determined from the dipole measurement, but since we know this ratio for the vapor, we can estimate the ratio for the liquid from our measurement of the change of intensity ratio of two Raman lines on liquefaction, one assigned to the trans molecule and the other to the gauche molecule. Using the value of $I(768)/I(666)$ stated above (5:1 for the vapor at 170°C and 1.8:1 for the liquid at 25°C),*** we have for the liquid at 25°C

$$N_g:N_t=1.3:1. \quad (4)$$

The preliminary measurement of the dipole moment of 1,2-dibromoethane was also carried out in the gaseous state, from which the energy difference ΔE between the trans and the gauche molecules of this substance can be calculated similarly:

$$\Delta E=1.4 \text{ kcal/mole}. \quad (5)$$

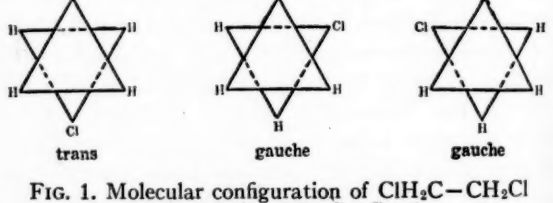

FIG. 1. Molecular configuration of ClH_2C-CH_2Cl as viewed along the C−C axis.

* This considerable change of energy difference can be explained by considering Onsager's reaction field in the liquid state (see Watanabe, Mizushima, and Masiko, Sci. Papers Inst. Phys. Chem. Research (Tokyo) **40**, 425 (1943)).

[4] Watanabe, Mizushima, and Morino, Sci. Papers Inst. Phys. Chem. Research (Tokyo) **39**, 401 (1942).

[5] Zahn, Phys. Rev. **38**, 521 (1931).

[6] The product of the principal moments of inertia is 2.012×10^6 for the *trans*-form and 2.647×10^6 for the gauche form in atomic weight-angstrom units. The frequencies of the skeletal vibrations which are the lowest and, therefore, the most important are 300, 223, 709, 754, 1052 cm^{-1} for the trans form and 265, 411, 654, 677, 1031 cm^{-1} for the gauche form. (See our paper published in Scientific Papers Inst. Phys. Chem. Research (Tokyo) **40**, 100 (1942).)

** The dipole moment m_t of the trans molecule is put equal to zero.

*** From the values of N_g/N_t and $I(768)/I(666)$ for the vapor we obtain the ratio $S(768)/S(666)$ of the scattered intensities of the *trans*- and the gauche molecules. Assuming the same value of $S(768)/S(666)$ for the liquid, we have the equilibrium ratio of Eq. (4).

INFRA-RED ABSORPTION

The infra-red spectra of 1,2-dichloroethane and 1,2-dibromoethane were measured in different states of aggregation (see Tables I and II). From the change of absorption intensities with temperature, especially those of the frequencies of 1236 cm^{-1} (the trans molecule) and 1297 cm^{-1} (the gauche molecule) of 1,2-dichloroethane in the gaseous state, the energy difference ΔE between the two kinds of isomeric molecules was calculated as

$$\Delta E = 1.03 \text{ kcal/mole.}$$

Similarly from the change of absorption intensities of the frequencies of 1192 cm^{-1} (the trans molecule) and 1236 cm^{-1} (the gauche molecule) of 1,2-dibromoethane in the gaseous state we obtain

$$\Delta E = 1.45 \text{ kcal/mole.}$$

These values of ΔE are in good agreement with those of Eqs. (3) and (5).

ELECTRON DIFFRACTION

Next we made the electron diffraction experiment of 1,2-dichloroethane in the gaseous state at 14°C.[7] The photographs showed eight measurable rings whose $s(s=4\pi/\lambda \sin\theta/2)$ values are given in Table III. These are then compared with the theoretical intensity curves calculated for the isomeric mixtures of various compositions (molar fractions of the gauche isomer 10 percent, 20 percent, 30 percent, 40 percent, 50 percent), of which the 20 percent curve corresponds most closely to the experiment.[8] This is the very composition which we should expect from our experimental result of dipole moment (18.8 percent at 14°C). Therefore the result of the electron diffraction experiment is in agreement with that hitherto obtained from other experimental researches of this series.

ENTROPY

The experiments described above have supplied us with almost all the important molecular data of the *trans*- and the gauche forms of 1,2-dichloroethane and their equilibrium ratio. We are now able to calculate the statistical entropy and to compare the result with the third law value obtainable from thermal measurement. This value for the vapor at 25°C under its own vapor tension (78.9 mm) was calculated as 78.23 e.u. from the entropy of the liquid 49.84 e.u. obtained by Pitzer[9] at the same temperature. The statistical entropy S' under the same condition was calculated from the moments of inertia and normal frequencies (except torsional frequencies) as 73.38 e.u. for the *trans*-form and 74.39 e.u. for the gauche form.[6] This refers, therefore, to the rigid molecular model and therefore, we have to add to it the entropy contributed by the torsional oscillation about the C−C bond as axis. If this is assumed to be the same for both kinds of isomeric molecules (S''), the statistical entropy of the actual

TABLE II. 1,2-Dibromoethane.

Raman effect		Infra-red absorption*		
Liquid	Solid	Gas	Liquid	Solid
	49 (3*b*)			
91 (2*b*)				
132 (2)				
190 (10)	190 (7)			
231 (3)				
325 (1)				
355 (5)				
469 (1)				
551 (8)				
583 (6*b*)				
660 (10*b*)	657 (10)			
		?	747 (st)	750 (med)
836 (2)		843 (med)	838 (st)	
899 (3)		897 (w)	897 (st)	
933 (2)	934 (1)			
997 (0)				
1019 (1)		1022 (w)	1022 (w)	
1053 (9)	1056 (5)			
		1057 (b. med)	1091 (b. st)	1087 (med)
1169 (3)				
		1192 (st)	1192 (st)	1192 (st)
1255 (10*b*)	1250 (8*b*)	1236 (st)	1256 (st)	
1276 (3)				
1419 (3)				
1440 (5)	1438 (3)	1455 (b. med)	1425 (b, st)	1440 (b. st)
2859 (4)	2857 (3)			
2953 (8)				
2972 (10)	2966 (10)			
3013 (4*b*)	3013 (5)			

* The infra-red absorption was measured in the frequency region between 700 and 1500 cm^{-1}.

TABLE III. *s*-values for the observed maxima and minima.

Maxima		Minima	
1	3.205 (strong)		
		1	4.141
2	4.940 (strong)		
		2	5.902
3	6.003 (weak)		
		3	6.664
4	7.699 (strong)		
		4	8.591
5	9.205 (medium)		
		5	9.993
6	10.598 (weak)		
		6	11.305
7	12.051 (strong)		
		7	13.189
8	14.813 (medium)		

[7] Yamaguchi, Morino, Watanabe, and Mizushima, Sci. Papers Inst. Phys. Chem. Research (Tokyo) **40**, 417 (1943).

[8] We have tentatively calculated the theoretical intensity curves for the mixtures of the trans and the cis isomers, but no curves for any reasonable compositions could explain the experimental result. The weak diffuse maximum for $S=6.003$ observed first by our experiment is especially important for the structural determination. The other maxima and minima are in good agreement with those observed by Beach and Palmer [J. Chem. Phys. **6**, 639 (1938)].

[9] Pitzer, J. Am. Chem. Soc. **62**, 331 (1940).

TABLE IV. *s*-values for the observed maxima and minima of $Cl \cdot H_2C-CCl_3$ and $Cl_2HC-CCl_3$.

ClH_2C-CCl_3				$Cl_2HC-CCl_3$			
Maxima		Minima		Maxima		Minima	
1	2.715			1	2.680		
		1	3.722			1	3.635
2	4.758			2	4.678		
		2	5.950			2	5.900
3	7.442			3	7.558		
		3	8.423			3	8.411
4	9.112			4	8.991		
		4	10.181			4	9.930
5	11.90			5	12.033		
						5	13.10
				6	14.154		
						6	15.4
				7	16.3		

mixture is calculated as

$$S=(S_T'+S'')x+(S_G'+S'')(1-x) \\ -Rx\ln x-R(1-x)\ln(1-x), \quad (6)$$

where the subscripts T and G refer to the trans and the gauche molecules, respectively and x denotes the molar fraction of the *trans*-isomer which is equal to 0.800 at 25°C. Substituting the said third law value 78.23 e.u. into S of Eq. (6), we have as the value of S''

$$S''=3.66 \text{ e.u.}$$

and if the torsional oscillation is assumed to be harmonic, the frequency ω is calculated as

$$\omega=90 \text{ cm}^{-1}.$$

Since this torsional frequency is obtained by a difference method, it is in error by the sum of the error in the statistical calculation and that in the thermal measurement. Moreover, we have assumed simply that the torsional frequencies for both molecular forms are the same. In view of this situation it is not unreasonable to identify the Raman line of the frequency of 125 cm^{-1} with the torsional oscillation of the gauche molecule. (The torsional oscillation of the trans molecule is not active in the Raman effect.)

Similar calculation was made for 1,2-dibromoethane. From the entropy of solid at 200°K (31.33 e.u.) obtained by Pitzer and the heat of sublimation (14075 cal/mole) measured by us the third law entropy of the vapor at the same temperature and under its own vapor pressure is calculated as 101.70 e.u.[10] The statistical entropy for the rigid molecular models amounts to 98.21 for the *trans*-form and 98.60 e.u. for the gauche form under the same condition.[10] The torsional frequency about the C−C bond as axis is then calculated as 83 cm^{-1} which is in agreement with the observed Raman frequency 91 cm^{-1} assigned to the gauche molecule.

MOLECULAR STRUCTURE OF ASYMMETRICAL TETRACHLOROETHANE AND PENTACHLOROETHANE

We have already stated in the section of the Raman effect that the molecule of the type X_3C-CH_2X has only one configuration. For the further confirmation of this conclusion we made the Raman measurement and electron diffraction experiment on asymmetrical tetrachloroethane Cl_3C-CH_2Cl and pentachloroethane $Cl_3C-CHCl_2$.

The Raman lines observed for asymmetrical tetrachloroethane in the liquid state are 118(5*b*), 157(5), 242(8), 308(7), 336(7), 381(9), 549(10), 718(6*b*), 747(3), 765(2), 813(9*b*), 859(3), 1056(5), 1202(4), 1281(4), 1420(6), 2961(9), 3017(8) cm^{-1} and those for pentachloroethane in the liquid state are 85(4*b*), 165(3), 174(3), 223(6), 238(6), 277(5), 324(8*b*), 404(10*b*), 428(1), 584(7*b*), 724(2), 772(1*b*), 818(5), 835(6), 856(0), 1020(4), 1210(2), 1254(2), 2986(5*b*) cm^{-1}. For both of these two substances practically the same results were obtained in the solid state.[11] From the number of the observed lines and the symmetry properties of these molecules it can be concluded that these substances have only one molecular form each. According to our view this form must correspond to the staggered configuration, in which the projection of one C−Cl or C−H line upon the plane perpendicular to the C−C axis is midway between those of two C−Cl lines in the other half of the molecule. That such is actually the case was proved by our electron diffraction experiment, whose *s*-values for the observed maxima and minima are shown in Table IV. These results are in good agreement with those of the theoretical intensity curves calculated for the said staggered form, but not with those calculated for the eclipse form in which the three C−X bonds (X=Cl or H) eclipse the three C−X bonds in the other half of the molecule as viewed along the central C−C axis. We therefore, have to consider that for the potential barrier hindering the internal rotation about the C−C bond as axis the repulsions between the chlorine atoms or polysubstituted ethanes is more important than the "overlapping effect" of wave functions, otherwise the eclipse form would become stable for these molecules.

[10] Odan, Mizushima, and Morino, Sci. Papers Inst. Phys. Chem. Research (Tokyo) **42**, 27 (1944).

[11] Mizushima, Morino, Kawano, and Ochiai, Sci. Papers Inst. Phys. Chem. Research (Tokyo) **42**, 1 (1944).

A Geometric Approach to the Theory of the Carbon-Carbon Bond*

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A geometric method of constructing the carbon-to-carbon bonds is described. It is postulated that there exists a region of high, constant electron density between the bound atoms. Calculations based on this postulate confirm it in that they lead to screening constants which are in fair agreement with the values given by Pauling and that plots of the variation of electron density with changes in the angular or radial variables reflect just such a region. Further, the plots are in good qualitative agreement with the well-known properties of rotation about a single bond and lack of rotation about a double bond.

IN a previous paper[1] a discussion was presented of the variation of electron density about tetrahedrally and trigonally hybridized carbon atoms. The treatment of directed valence there presented suggests the possibility of a simple and fruitful geometric approach to the problem of the chemical bond. In the present paper, only the commonest carbon-to-carbon bonds will be considered. Even these cases are simplified, perhaps idealistically, by regarding the possible other bonds which the carbon atoms may sustain as having no influence on the bond in question. Polarization effects in a bond will, of course, require corrective factors, whether these effects be due to adjacent bonds or to different electronegativities in the atoms joined. But such corrections will only serve to complicate the calculations; the essential features can best be presented without introducing those refinements.

To recapitulate briefly, the model upon which the reasoning is based is as follows: a sphere whose radius is arbitrarily taken as that at which a maximum electron density is attained. Upon the surface of this sphere, therefore, there are centers of maximum density whose relative location is determined by the state of "hybridization" of the hydrogen-like orbitals of the atom. For tetrahedral carbon, these centers are of equal density and are located at tetrahedral angles with respect to one another, while for trigonal carbon there are three centers of equal density located in a plane at intervals of 120° around the atomic core, plus two other centers of lesser density located within the sphere whose surface contains the first three and at right angles to the plane of those three. Upon moving away from these centers in any direction, the density will be found to diminish in accordance with the properties of the wave functions studied in the previous paper.

Now the concept that the formation of a bond requires overlapping of orbitals from the participating atoms has long been well established.[2] Thus, it is considered that a chemical bond between two such atoms as have been described involves their mutual approach until their two electron clouds interact in such a way as to impart a maximum stability to the system. A very convenient and reasonable way to look at this is to consider the condition of maximum stability as obtaining when there exists in the region between the two atoms a space where the density of electrons is substantially constant. This space constitutes a region of electrical homogeneity. In order to break this bond and separate the two atoms, it will be necessary to disrupt this homogeneity—a process which will consume energy in an amount increasing with the extent of the disruption. The energy so consumed should closely correspond to the quantity which is termed the energy of the bond.

In a system in which polarization forces are either non-existent or equally balanced about a bond between two atoms, A and B, it is to be expected that along the axis between these atoms there should be an interval through which the summation of electron contributions of the two atoms will show a negligible variation. Two well-defined points within this interval may be picked, one being the midpoint, a, at which the radius is that measured experi-

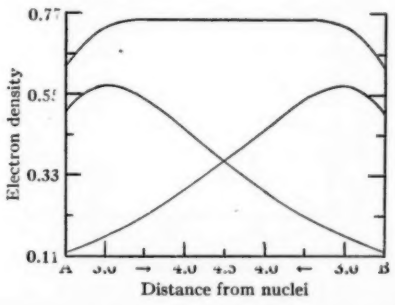

FIG. 1. Variation of electron densities with distances from atomic cores in an unpolarized bond between two tetrahedrally hybridized carbon atoms. Atomic units given are in terms of Zr/a_0. The midpoint of the total AB abscissa represents the midpoint of the bond.

* This material is taken from a thesis presented by the author to the Graduate School of the University of Oregon in partial fulfillment of the requirements for the Ph.D. degree in chemistry.

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[1] H. K. Zimmerman, Jr. and P. Van Rysselberghe, J. Chem. Phys. 17, 598 (1949).

[2] See for example S. Glasstone, *Theoretical Chemistry* (D. Van Nostrand Company, Inc., New York, 1944), pp. 107–12.

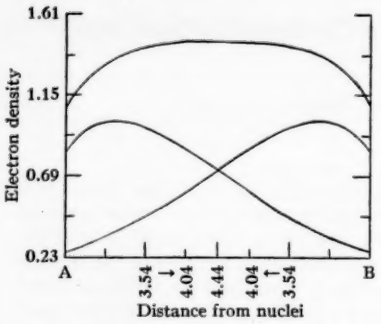

FIG. 2. Variation of electron densities with distances from atomic cores in an unpolarized bond between two trigonally hybridized carbon atoms. Atomic units are given in terms of Zr/a_0. The midpoint of the total AB abscissa represents the midpoint of the bond.

mentally, and the other, b, being that at which the radius from one of the atomic cores, say A, is equal to the extremal value.[1] The distance of this second point from the core of atom B may then be easily expressed as a function of these two parameters. Then, making use of probability distribution functions,[3] one may write

$$D_a = D_b, \tag{1}$$

where D_a is the density at point a (the sum of equal contributions from atoms A and B), and D_b is the density at point b (the sum of the contribution from atom A and a lesser contribution from atom B).

Thus, in the case of the bond between two tetrahedral carbon atoms,

$$D_a = D_{aA} + D_{aB} = 2D_{aA}, \tag{2}$$

where D_{aA} is the density at point a contributed by atom A, while that contributed by atom B is D_{aB}. Since the two contributions are equal at the midpoint between the two nuclei, the second equality is obvious. At point b, a similar expression may be

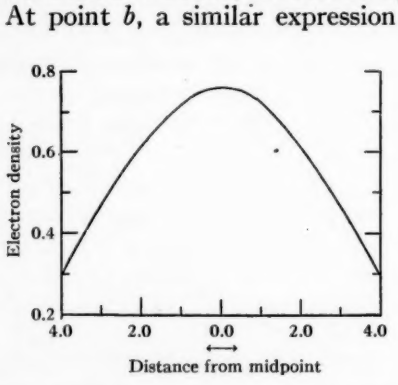

FIG. 3. Variation of electron densities with variation of the angle, θ_1, keeping all other angles constant. Distances are measured along a line parallel to the z axis and passing through the midpoint of the internuclear axis, for the tetrahedral carbon-carbon bond. Atomic units given are in terms of Zr/a_0.

[3] L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1935), p. 139.

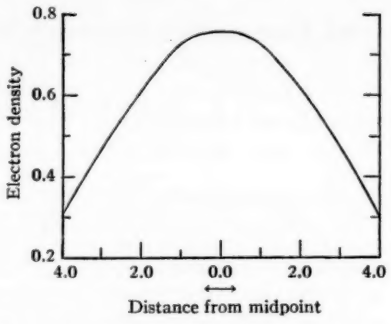

FIG. 4. Variation of electron densities with variation of the angle, ϕ_1, keeping all other angles constant. Distances are measured along a line perpendicular to the z axis and to the internuclear axis, and passing through the midpoint of the internuclear axis, for the tetrahedral carbon-carbon bond. Atomic units given are in terms of Zr/a_0.

written:

$$D_b = D_{bA} + D_{bB}, \tag{3}$$

where the notation is analogous. Here, however, the contributions of the two atoms, A and B, are unequal, so that we must retain the explicit sum.

In the case of the double bond (between two trigonal carbons) entirely analogous expressions may be written. It, must, however, be remembered that, for example,

$$D_{aA} = D_{aA_t} + D_{aA_p}, \tag{4}$$

wherein D_{aA_t} is the contribution of the trigonal orbital of atom A, and D_{aA_p} is that of the p_z orbital. Clearly, D_{aA_p} is zero along the internuclear axis because of the effect of the angular variable which it contains, but at any point above or below the plane of the trigonal orbitals, it makes a definite contribution which must be included.

All these densities may be readily expressed in terms of functions previously given,[1] it being remembered that the tetrahedral function to be considered is a four electron function, while the trigonal function is a three electron function. Thus, in order to have comparable single electron functions with which to work, we take the fourth root of our total tetrahedral function, $(\psi_{tet})^{\frac{1}{4}}$, and the cube root of our total trigonal function, $(\psi_{tri})^{\frac{1}{3}}$. In order to be entirely precise and general, the densities which we then obtain should be written as integrals of these single electron functions over the whole of the space encompassing the bond. But because of the great difficulty in evaluating such integrals, we have introduced the approximation of mapping only the probability distribution functions at a number of successive points. Thus, we write for the "density" at point a in the tetrahedral bond, the expression

$$D_a = 2D_{aA} = 2((\psi_{tet})^{\frac{1}{4}})^2, \tag{5}$$

and analogous expressions for D_b (tetrahedral) and D_a and D_b (trigonal).

In the expressions for the forementioned functions, there still occurs the undetermined parameter, Z, which is the effective positive charge on the core of the atom under consideration. Thus, the expansion of Eq. (1) for either the trigonal case or the tetrahedral one turns out to be a complicated expression in Z as the unknown. The solution of this expression is somewhat laborious, since the form of the equation requires that it be performed graphically; however, since the procedure is straightforward, space will not be consumed to present it in detail here. By this method, it has been calculated that, for tetrahedral and trigonal carbon, respectively,

$$Z=3.09, \tag{6}$$

$$Z=3.50. \tag{7}$$

These values correspond respectively to screening constants of 0.3 and 0.25 for the electrons in the "hybridized" systems. They are thus in fair agreement with the approximate screening constant of 0.4 electron units given by Pauling[4] and so tend to confirm the correctness of the reasoning.

Employing the values for Z just given, it is now possible to calculate numerical values for the sums of probability distribution functions (expressed by Eqs. (2) and (3) and their analogs) in the bond between two unpolarized tetrahedral carbon atoms and between two unpolarized carbon atoms in the sort of double bond first suggested by Hückel,[5] at any desired radius along the internuclear axis. Such values have been calculated at a number of points, and it is found that they follow curves like those shown in Fig. 1 for the tetrahedral bond and in Fig. 2 for the double bond. In each of these figures, the two lower curves are radial variations of the probability distribution functions (i.e., electron density number) for the separate atoms, while the upper curve represents the summation of the two contributions to electron density. The manner in which the nearly linear portions of the curves from the individual atoms combine to give a high, constant density over a very considerable range furnishes a striking confirmation of the original hypothesis.

The confirmation is strengthened if one examines the effect of a variation in one or another of the angular coordinates of each of the atoms in the bond. In Figs. 3 and 4 there are shown, respectively, the summed densities obtained by varying θ_1 and ϕ_1 about the extremal values previously given,[1] during each variation keeping all other angular parameters constant at the extremal values. The axis on which the sums are taken is a line perpendicular to the internuclear axis. Thus, in Fig. 3, the variation may be considered to be along a line parallel to the p_z axis of maximum density. At large variation of θ_1 from its maximum value, the density of electrons is seen to be relatively low. But as the maximum value is approached, this density on the line chosen for consideration increases continually until at last it is seen that there is a fairly considerable region of high and constant density in the neighborhood of the midpoint on the internuclear axis (i.e., the maximum value of θ_1). Similarly, in Fig. 4, the variation is along a line in the x, y plane and perpendicular to the internuclear axis. The variation in density with changes in ϕ_1 is then seen to behave in just the same way as it does with the changes in θ_1. The results of parallel calculations for the Hückel double bond are presented in Figs. 5 and 6 and are also seen to be in agreement with the hypothesis.

A further interesting result may be observed in the matter of the angular symmetry reflected by Figs. 3 and 4, wherein the curves are virtually identical even though the planes of the angular coordinates being varied are mutually perpendicular, in contrast to the obvious lack of such symmetry shown by Figs. 5 and 6, wherein variations on the mutually perpendicular planes of the angular coordinates lead to very different curves. Thus it appears that a rotation of 90° in one atom with respect to the other involves no alteration of electron density

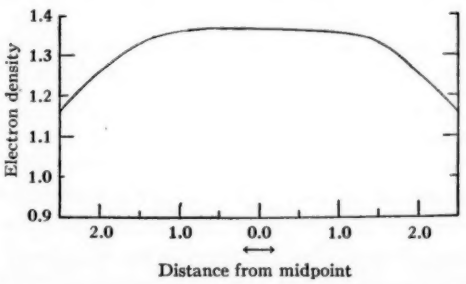

FIG. 5. Variation of electron densities with variation for the Hückel double bond of the angle, θ_1, keeping all other angles constant. Distances are measured along a line parallel to the z axis and passing through the midpoint of the internuclear axis. Atomic units given are in terms of Zr/a_0.

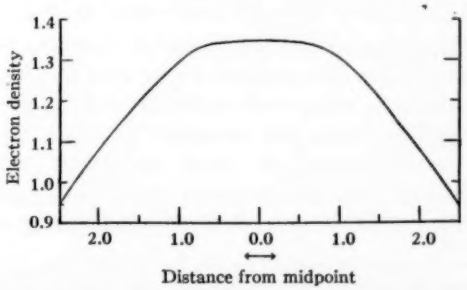

FIG. 6. Variation of electron densities with variation for the Hückel double bond of the angle, ϕ_1, keeping all other angles constant. Distances are measured along a line perpendicular to the z axis and to the internuclear axis, and passing through the midpoint of the internuclear axis. Atomic units given are in terms of Zr/a_0.

[4] L. Pauling, *Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1944), p. 65.
[5] E. Hückel, Zeits. f. Physik. 60, 423 (1930).

within the tetrahedral bond, while such a rotation requires a very substantial alteration of electron density within the double bond. The symmetry shown for the tetrahedral bond is therefore in agreement with the physical fact that there exists freedom of rotation about such a bond; every angular orientation achieved by rotating on the internuclear axis is identical in electron density with every other, and as a consequence no expenditure of energy is needed to accomplish rotation. This, of course, does not consider steric hindrance to rotation which may arise through the potential fields of substituents on the two carbon atoms. In the double bond, on the other hand, Figs. 5 and 6 illustrate a marked lack of symmetry. Thus, any rotation about that bond will require an alteration of the electron distribution and so an expenditure of energy which will make such a rotation very difficult to achieve. This, too, is in agreement with the well-known fact that rotation about a double bond is never accomplished except by the most extraordinary means.

ACKNOWLEDGMENTS

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Directed Valence as a Property of Determinant Wave Functions*

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Making use of Slater's extension of the Heitler-London method, it is shown that the directional properties of carbon valences are a logical consequence of the combination of the hydrogen-like individual electron orbitals of carbon into a determinant wave function. It is possible to separate the radial and angular parts of such a function by factoring. Partial differentiation of the factored function with respect to the angular variables leads to proof of the directional properties, while partial differentiation with respect to the radial variable shows that, as long as all valence electrons are at equal distances from the nucleus, the electron density is maximum at points located on a sphere whose radius is calculated.

FOR many years, Pauling's theory of directed valence[1] has been used with much success. However, his derivations require the use of certain postulated rules, the construction of successive linear combinations of one-electron wave functions (the first of which in the case of the carbon valences is assumed to contain contributions from only two of the four one-electron functions), the complete neglect of the influence of radial factors, etc. While these points do not invalidate the results of the calculations, they do tend somewhat to obscure the fundamental nature of the directed valence concept. Recently, there was published a paper[2] in which it is shown that the phenomenon of directed valence can be proved without the necessity of such assumptions. At the time this paper appeared, we were engaged in a calculation which parallels it, and since the mathematical equipment which we have chosen is considerably simpler than the vector notation used by Artmann, it is considered that the treatment which is presented hereinafter represents an improvement over his derivation. In addition to this simplification in the mathematics, we have been able to show explicitly that radial factors need not be neglected in the present procedure and that they do not, in fact, influence the directional properties of the valences.

Since Artmann has already discussed numerous examples, we shall restrict ourselves mainly to the cases presented by tetrahedral carbon and by carbon as it occurs in the double bond. However, in order to make completely clear the principles of the method, we shall first consider the simplest possible case—that of the configuration, $p_x p_y$, as for example it occurs in the ^3P state of oxygen. Employing the Slater extension of the Heitler-London method,[3] the system of the two unpaired electrons may be written as the determinant,

$$\psi = \eta \begin{vmatrix} p_{x1} & p_{x2} \\ p_{y1} & p_{y2} \end{vmatrix} \tag{1}$$

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[1] L. Pauling, J. Am. Chem. Soc. **53**, 1367–1400 (1931).

[2] K. Artmann, Zeits. f. Naturfor. **1**, 426–32 (1946).

[3] J. C. Slater, Phys. Rev. **38**, 1109 (1931).

in which ψ is the wave function for the composite system, η is the normalization factor required by the combination of one-electron wave functions as a two-electron determinant wave function (*vide* infra), while p_x and p_y are the normalized one-electron hydrogen-like wave functions corresponding respectively to the sets of quantum numbers $n=2$, $l=1$, $m=1$ and $n=2$, $l=1$, $m=-1$, the subscripts 1 and 2 referring to the coordinates of the two electrons. The spins of the two electrons are taken parallel to each other. By substituting into Eq. (1) the explicit hydrogen-like wave functions and factoring out of the determinant the constants and radial factors (corresponding to equal values of the distances from the electrons to the center of the nucleus), one arrives at the expression,

$$\psi=\eta\left(\frac{1}{4(2\pi)^{\frac{1}{2}}}\right)^2 \times\left(\frac{Z}{a_0}\right)^3\rho^2\exp\rho\begin{vmatrix}\sin\theta_1\cos\phi_1 & \sin\theta_2\cos\phi_2\\ \sin\theta_1\sin\phi_1 & \sin\theta_2\sin\phi_2\end{vmatrix}, \quad (2)$$

where Z is the effective atomic number of the atomic core; a_0 is the radius of the first Bohr orbit, 0.529 angstrom and ρ, θ_2, θ_1, ϕ_2, and ϕ_1 are the spherical polar coordinates of the respective electrons, with

$$\rho=Zr/a_0, \quad (2a)$$

r being the actual radial coordinate in angstroms.

In order to establish the values of θ_1, θ_2, ϕ_1, and ϕ_2 at which ψ is an extremum, one now calculates the partial derivatives of ψ with respect to the θ's and ϕ's, equating each derivative to zero. This procedure leads to the system of four equations,

$$\left.\begin{aligned}
\frac{\partial\psi}{\partial\theta_1}&=\begin{vmatrix}\cos\theta_1\cos\phi_1 & \sin\theta_2\cos\phi_2\\ \cos\theta_1\sin\phi_1 & \sin\theta_2\sin\phi_2\end{vmatrix}=0\\
\frac{\partial\psi}{\partial\phi_1}&=\begin{vmatrix}-\sin\theta_1\sin\phi_1 & \sin\theta_2\cos\phi_2\\ \sin\theta_1\cos\phi_1 & \sin\theta_2\sin\phi_2\end{vmatrix}=0\\
\frac{\partial\psi}{\partial\theta_2}&=\begin{vmatrix}\sin\theta_1\cos\phi_1 & \cos\theta_2\cos\phi_2\\ \sin\theta_1\sin\phi_1 & \cos\theta_2\sin\phi_2\end{vmatrix}=0\\
\frac{\partial\psi}{\partial\phi_2}&=\begin{vmatrix}\sin\theta_1\cos\phi_1 & -\sin\theta_2\sin\phi_2\\ \sin\theta_1\sin\phi_1 & \sin\theta_2\cos\phi_2\end{vmatrix}=0
\end{aligned}\right\}. \quad (3)$$

The solution of this system leads to the result that ψ is an extremum[4] when the angular coordinates of the two electrons are such as to give a bond angle of 90°. However, while the condition involving the first partials is a necessary condition which must be satisfied to show existence of an extremum, it is not necessarily sufficient. In order to have unequivocaproof, it should, if possible, be shown that the del terminant of all second partials of ψ is not zero. Thus, using the general notation, κ, for all the angular variables,

$$\left|\frac{\partial^2\psi}{\partial\kappa_n\partial\kappa_m}\right|>0 \qquad \begin{matrix}n=1,2,3,4,\\ m=1,2,3,4,\end{matrix}$$

indicates the angular values calculated give a minimum, while

$$\left|\frac{\partial^2\psi}{\partial\kappa_n\partial\kappa_m}\right|<0 \qquad \begin{matrix}n=1,2,3,4,\\ m=1,2,3,4,\end{matrix}$$

indicates that they give a maximum. If we take as the solution of the system of equations, (3), the values,

$$\begin{aligned}\theta_1&=90^\circ \quad \phi_1=0^\circ\\ \theta_2&=90^\circ \quad \phi_2=90^\circ;\end{aligned} \quad (4)$$

however, it is found that the determinant is identically zero. Therefore, it is necessary to fall back upon a less satisfactory method of trial and error to show that the results, (4), give an extremum. This can be done by introducing a small variation into one of the angular values which have been calculated, while keeping the other values as previously found. When this is done and the value of the determinant in Eq. (2) calculated for a number of such variations, it is found that all these result in a lower value of the determinant than is found with the values, (4). Hence, it may reasonably be concluded that the values given do actually result in a maximum.

A further way in which the same result may be shown is the following.† In the present simple example, the determinant of Eq. (2) may be readily expanded to the form

$$\psi=F(\rho)(\sin\theta_1\cos\phi_1\sin\theta_2\sin\phi_2 -\sin\theta_1\sin\phi_1\sin\theta_2\cos\phi_2).$$

This is identically equal to

$$\psi=F(\rho)(\sin\theta_1\sin\theta_2\sin(\phi_2-\phi_1)).$$

It is therefore obvious that the maximum value of the angular function occurs for the angles given in (4). Thus one is able immediately to see that the function actually depends only on the three variables, θ_1, θ_2, $(\phi_2-\phi_1)$; i.e., ϕ_1 and ϕ_2 are not independent of each other, and the function is maximum for $\theta_1=\theta_2=\phi_2-\phi_1=90^\circ$.

Considering now the tetrahedral carbon atom, we apply the Slater extension of the Heitler-London method to the ^5S state into which the carbon atom

[4] Cf. H. Hancock, *Theory of Maxima and Minima* (Ginn and Company, Boston, 1917), pp. 79–82.

† This point was indicated by the reviewer of this article, to whom the authors wish to express their thanks.

may be considered to have been thrown by the process of approaching chemical combination. Hence, we have the composite system as the determinant,

$$\psi_{\text{tet}}=\eta^{\frac{1}{2}}\begin{vmatrix} s_1 & s_2 & s_3 & s_4 \\ p_{x1} & p_{x2} & p_{x3} & p_{x4} \\ p_{y1} & p_{y2} & p_{y3} & p_{y4} \\ p_{z1} & p_{z2} & p_{z3} & p_{z4} \end{vmatrix} \tag{5}$$

in which η is again a normalizing factor.[5] It should be noted that such a determinant as (5) is the only way of building a four electron wave function which is antisymmetrical with respect to each of the four electrons: permutation of any two columns changes the sign of the function.

Substituting into Eq. (5) the expressions for the hydrogen-like wave functions, and factoring out the constants and radial factors (corresponding again to equal values of the distances of the four electrons from the center of the nucleus),

$$\psi_{\text{tet}}=\eta^{\frac{1}{2}}(1/4(2\pi)^{\frac{1}{2}})^4(Z/a_0)^6\rho^3(2-\rho)\exp(-2\rho)$$
$$\times\begin{vmatrix} 1 & 1 & 1 & 1 \\ \sin\theta_1\cos\phi_1 & \sin\theta_2\cos\phi_2 & \sin\theta_3\cos\phi_3 & \sin\theta_4\cos\phi_4 \\ \sin\theta_1\sin\phi_1 & \sin\theta_2\sin\phi_2 & \sin\theta_3\sin\phi_3 & \sin\theta_4\sin\phi_4 \\ \cos\theta_1 & \cos\theta_2 & \cos\theta_3 & \cos\theta_4 \end{vmatrix}. \tag{6}$$

The special case, $\rho_1=\rho_2=\rho_3=\rho_4=\rho$, makes the study of the angular behavior of the function, ψ_{tet}, particularly convenient. The experimental equivalence of the four carbon bonds, as in methane, for instance, indicates that the four ρ's have equal time averages and provides a justification for our procedure.

It is now necessary to determine the values of the θ's and ϕ's which simultaneously cause the partial derivatives of ψ_{tet} with respect to each of the eight angular variables to vanish. These values will then include those of the eight variables which make the function an extremum.[4] Thus, again using the general notation, κ_n, to denote the θ_n and ϕ_n, our problem is to calculate the partials, $\partial\psi_{\text{tet}}/\partial\kappa_n$, and to equate them to zero. Here, even more than in the preceding simple example, the operation is substantially simplified because of the fact that the particular angles, κ_n, are all in a single column of the determinant. Thus, for instance, the expression for the partial derivative of ψ_{tet}, as given in Eq. (6), with respect to θ_1 can be equated to zero as follows:

$$0=\eta^{\frac{1}{2}}(1/4(2\pi)^{\frac{1}{2}})^4(Z/a_0)^6\rho^3(2-\rho)\exp(-2\rho)$$
$$\times\begin{vmatrix} 0 & 1 & 1 & 1 \\ \cos\theta_1\cos\phi_1 & \sin\theta_2\cos\phi_2 & \sin\theta_3\cos\phi_3 & \sin\theta_4\cos\phi_4 \\ \cos\theta_1\sin\phi_1 & \sin\theta_2\sin\phi_2 & \sin\theta_3\sin\phi_3 & \sin\theta_4\sin\phi_4 \\ -\sin\theta_1 & \cos\theta_2 & \cos\theta_3 & \cos\theta_4 \end{vmatrix}. \tag{7}$$

Thus it is seen that the mathematical process of differentiating the composite wave function to determine its extremal angles, although a formidable task were the function an arbitrary sum-and-product relation of the eight angular variables, is very greatly facilitated by the use of the determinant. Hence, the determinant not only affords a convenient method of mathematically expressing the interchangeability of the electrons of the composite system, but it also makes possible an easy and straightforward analysis of the problem once it is stated by means of Eqs. (5) and (6).

This procedure yields a set of eight simultaneous equations in eight unknowns. In principle, the set might be solved analytically to give the eight extremal values of the θ's and ϕ's. However, such a procedure is an extremely complex undertaking, and it has been found more feasible to assume certain sets of values for these variables, testing them in the set of eight equations to determine whether they satisfy the system. In this manner, it is found that a set of variables describing four functions at tetrahedral angles with respect to one another does indeed satisfy the condition imposed. Numerically, these may be taken as follows:

$$\begin{aligned} \theta_1&=54^\circ\,44' & \phi_1&=0 \\ \theta_2&=125^\circ\,16' & \phi_2&=\pi/2 \\ \theta_3&=54^\circ\,44' & \phi_3&=\pi \\ \theta_4&=125^\circ\,16' & \phi_4&=3\pi/2. \end{aligned} \tag{8}$$

One can readily verify that twice 54° 44′ is 109° 28′, i.e., the tetrahedral angle. Also, 125° 16′ is the difference between 180° and 54° 44′, and thus the positions thereby selected for the four tetrahedral directions are obvious. The important point which the theory shows is that the condition of mutual tetrahedral orientation gives an extremum. This important circumstance is not immediately obvious from Eq. (5), since an expression of the form of (1) or (5) is actually invariant with respect to rotation of the coordinate axes.

Now the condition stated above is a necessary

[5] In our actual calculations, we have normalized the function to four—unity for each electron in the system. Such a normalization expresses the fact that the total charge of the distribution represented by the four-electron function is that of four electrons. This type of normalization is useful when comparisons are to be made between functions involving different numbers of electrons, as will be the case later in the present paper. Further, when such composite functions are employed, as will be done in a subsequent paper, in the discussion of electron distributions in bonds, it is easy to show that, as a matter of fact, the normalization to four is very little different, in its influence on the numerical values obtained, from the more usual normalization to unity. Although it is not a complete or accurate way of treating the problem, normalization to four here is, in effect, simply a way of taking into account the repulsion of a given electron in the system by the other three, i.e., the density of distribution is somewhat greater in the bond direction with this normalization to four than with the normalization to unity. However, since this step does not affect the present demonstration of the angular properties, it may, if desired, be regarded merely as an arbitrary constant for the purpose of this paper. Similar remarks, with a normalization to three, also apply to the trigonal system discussed later in this paper.

requirement for an extremum. Its sufficiency in this case is demonstrated by the fact that the determinant of all second partials of ψ_{tet} is negative. Thus,

$$\left|\frac{\partial^2\psi}{\partial\kappa_n\partial\kappa_m}\right|<0 \qquad \begin{matrix} n=1,2,\cdots,8 \\ m=1,2,\cdots,8 \end{matrix}$$

In the case of the double bond, the theory first proposed by Hückel[6] states that this bond consists of two parts: a secondary portion which consists of unhybridized $2p_z$ orbitals, and a primary portion which consists of a hybrid of the remaining three hydrogen-like orbitals of the outer shell of the carbon atom. This hybrid corresponds to what is often designated as "trigonal quantization." It gives the directional properties to the bond. In the same manner as before, this "hybrid" can be formulated as a composite function in the following way:

$$\psi_{tri}=\eta^{\frac{1}{2}}(1/4(2\pi)^{\frac{1}{2}})^3(Z/a_0)^{9/2}\rho^2(2-\rho)\exp(-3\rho/2)$$
$$\times\begin{vmatrix} 1 & 1 & 1 \\ \sin\theta_1\cos\phi_1 & \sin\theta_2\cos\phi_2 & \sin\theta_3\cos\phi_3 \\ \sin\theta_1\sin\phi_1 & \sin\theta_2\sin\phi_2 & \sin\theta_3\sin\phi_3 \end{vmatrix}, \quad (9)$$

in which η is once more a normalizing factor.[5]

Determination of the parameters, θ_n and ϕ_n, follows the same pattern as before, one set of values which simultaneously set the six first partial derivatives equal to zero being found to be

$$\begin{matrix} \theta_1=\pi/2 & \phi_1=0 \\ \theta_2=\pi/2 & \phi_2=2\pi/3. \\ \theta_3=\pi/2 & \phi_3=4\pi/3 \end{matrix} \quad (10)$$

However, as in the first case presented in this paper, calculation of the value of the determinant of second partial derivatives yields zero. But by introducing a moderate variation into the values of θ_1 and ϕ_1, meanwhile keeping all the other values at the figures given in (10), the value of the determinant can be calculated for a number of cases. Such calculations have shown that all such cases give values lower than that found from the combination, (10). This may be taken as presumptive evidence that the angles do determine a maximum.

Moreover, as in the case of ^3P oxygen discussed above,† the determinant of Eq. (9) may be expanded, and the appropriate identities used, to obtain the expression

$$\psi_{tri}=(\sin\theta_1\sin\theta_2\sin(\phi_2-\phi_1)+\sin\theta_2\sin\theta_3\sin(\phi_3-\phi_2)$$
$$+\sin\theta_3\sin\theta_1\sin(\phi_1-\phi_3))f(\rho).$$

From this it is again clear that the function is maximum when the θ's are all 90°, the foregoing expression then reducing to

$$\psi_{tri}=(\sin x+\sin y-\sin(x+y))f(\rho),$$

where

$$x=\phi_2-\phi_1,$$
$$y=\phi_3-\phi_2.$$

Thus it is once again apparent that, since only the differences of the ϕ's are significant, the number of independent variables among the ϕ's is once more reduced by one. This circumstance serves to indicate the reason for the difficulty encountered in showing the existence of extrema in two of the three cases studied, by the use of determinants only. However, the determinant treatment has been preserved throughout because of the advantages which it offers in the more complex cases, of which the tetrahedral is an example.

This last case presents, perhaps more forcibly than does that of the tetrahedral carbon, the distinction between the angular invariance of the composite wave functions and the fact—which is of such great importance chemically—that the angle between any given pair of "hybridized" valences possesses an optimum value which causes the composite function to assume a maximum value.

From an inspection of the form of Eqs. (6) and (9), it becomes apparent that the positions of the angular extrema determined through the method of partial derivatives are unaffected by the radial factors so long as those factors are the same for each of the four electrons and so can be factored. If now the angular variables are held constant, Eq. (6) may be written as

$$\psi_{tet}=K(Z/a_0)^6\rho_{tet}^3(2-\rho_{tet})\exp(-2\rho_{tet}), \quad (11)$$

and Eq. (9) may be written as

$$\psi_{tri}=k(Z/a_0)^{9/2}\rho_{tri}^2(2-\rho_{tri})\exp(-3\rho_{tri}/2). \quad (12)$$

Now, in general the differential element of the electron distribution about the atomic core corresponding to the "hybrid" function, ψ, may be written as

$$\psi^2\prod_1^n\rho_n^2d\rho_nds_n \quad (13)$$

in which each differential ds_n is an element of surface area on the unit sphere.

In order to make use of the angular extrema calculated above, we shall restrict ourselves to a consideration of small elements of solid angle, which are defined by the ds_n, in the extremal directions. In order to give physical meaning to the concept of distribution in such an element, it is necessary that the element be of a constant angular opening. Thus, within the limits of the physical model which we are considering, the four factors, ds_n, are equal to one another and constant. This has the effect of fixing

[6] E. Hückel, Zeits. f. Physik. **60**, 423 (1930).

the size of the solid angle with which we are dealing in any particular direction.

Since it has been seen that the angular extrema are unaffected by the radial factors for a function of the type of Eq. (6) and Eq. (9), it is reasonable to expect that the inverse statement also is true. Hence, let us hold all the angular factors in expression (13) equal to some constant value (say an extremal value) for the present. This places us within the confines of some element of solid angle. Further, we shall set all the $d\rho_n$ constant, in effect prescribing thereby the depth of the four volume elements whose product is given by (13). The precise value given to $d\rho_n$ need not concern us. The size of these volume elements will now vary with ρ^2 only. The radial distribution functions are then given by the expressions,

$$K'\rho_{\text{tet}}{}^{14}(2-\rho_{\text{tet}})^2 \exp(-4\rho_{\text{tet}}) \tag{14}$$

for the tetrahedral system, and

$$k'\rho_{\text{tri}}{}^{10}(2-\rho_{\text{tri}})^2 \exp(-3\rho_{\text{tri}}) \tag{15}$$

for the trigonal hybrid. In order to find the respective ρ which make these distribution functions maximum, we then take the derivatives of (14) and (15) with respect to their ρ, set each of these derivatives equal to zero, and solve for ρ. The extremal values of ρ found by this procedure are

$$\rho_{\text{tet}}=4.414, \tag{16}$$

$$\rho_{\text{tri}}=4.53. \tag{17}$$

It is interesting to note that these values are nearly equal to each other. The actual values of $(\psi_{\text{tet}})^{\frac{1}{2}}$ and $(\psi_{\text{tri}})^{\frac{1}{2}}$ at the ρ's, θ's and ϕ's giving extrema should be similar for justification of normalization[5] to four and three.

It might be pointed out that, whenever the ρ's of the various electrons are taken equal to one another, the complete four- or three-electron wave function is maximum for the values of ρ_{tet} and ρ_{tri} given by (16) and (17) regardless of the values chosen for the angular variables. In other words, regardless of the values given to the angles, the wave function is maximum for those angles when the four or three electrons are on the sphere corresponding to $\rho_{\text{tet}}=4.414$ or $\rho_{\text{tri}}=4.53$, the maximum of all these maxima occurring for the tetrahedral or trigonal configuration.

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The Formula of Uranyl Ion*

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The exchange of oxygen between uranyl ion and water was studied using oxygen 18 as a tracer. The results showed that the formula of uranyl ion in dilute hydrochloric acid solution is UO_2^{++}, neglecting any anion complexing, as distinguished from $U(OH)_4^{++}$, unless in $U(OH)_4^{++}$ two of the oxygen atoms are much more weakly bonded than the other two. The UO_2^{++} ion is covalently bonded in dilute hydrochloric acid solution as well as in crystalline uranyl chloride. The Raman spectrum of uranyl perchlorate was measured and the available Raman spectra of uranyl salts are interpreted considering the effects of complex ion formation.

FOR some time it has been generally assumed that uranyl ion is a doubly positive charged ion in acid solution. Freezing point studies[1] of uranyl chloride and uranyl nitrate have shown that they behave as completely dissociated ternary electrolytes. Isopiestic vapor pressure measurements[2] have shown that uranyl nitrate is a completely dissociated 1–2 electrolyte. Best, Taub, and Longsworth[3] measured the pH of uranyl chloride solutions up to 0.5 M concentration and found that very little

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** Present address, California Research Corporation, Richmond, California.
[1] C. Dittrich, Zeits. f. physik. Chemie 29, 449 (1899).
[2] R. A. Robinson, J. W. Wilson, and H. S. Ayling, J. Am. Chem. Soc. 64, 1469 (1942).
[3] R. J. Best, D. Taub, and L. G. Longsworth, Manhattan District Report CCA 380 (Nov. 1942).

TABLE I. The number of moles of O^{16} and O^{18} in water and uranyl chloride.*

	O^{16}	O^{18}
H_2O	pN_1^{16}	pN_1^{18}
$UO_2Cl_2 \cdot qH_2O$	$qsN_2^{16}+2sN_2^{16}$	$qsN_2^{18}+2sN_2^{18}$

* N_1^{16}, N_1^{18} mol fraction of O^{16}, O^{18} present in water before mixing; N_2^{16}, N_2^{18} mol fraction of O^{16}, O^{18} present in uranyl chloride before mixing; p moles of water to be mixed with s moles of salt.

hydrolysis of uranyl ion occurred. They also showed by electrometric and conductimetric titration of UO_3 with HCl that a sharp endpoint was obtained at two moles of acid per mole of base, corresponding to the ion UO_2^{++} or $U(OH)_4^{++}$. These results were obtained at uranyl concentrations below 0.1 *M* and from 10^{-3} *M* to 0.1 *M* HCl. No evidence was obtained to substantiate the existence of any appreciable concentration of $U(OH)_3^{+++}$ in the range of acid concentrations studied.

These investigations show that uranyl ion exists as a doubly charged positive ion in dilute acid solution; however they do not distinguish in any way between the ions UO_2^{++} or $U(OH)_4^{++}$. In 1940 Coulter, Pitzer, and Latimer[4] measured the entropy of uranyl ion and found it to be −17 e.u. They suggested that this value was unreasonably low as compared to other large dipositive ions such as $Ba^{++}(S^0Ba^{++}=3)$. Assuming that UO_2^{++} is the correct formula, it must be concluded that uranyl ion holds water molecules with stronger or more specific forces than an ion like Ba^{++}. The entropy of $U(OH)_4^{++}$ was calculated to be 16 e.u., which would appear to be more reasonable with respect to other ionic entropies. These entropy measurements, while suggestive, provide no basis for distinguishing between UO_2^{++} and $U(OH)_4^{++}$.

The Raman spectra of saturated solutions of various uranyl salts have been measured by Conn and Wu[5] and Satyanarayana.[6] The interpretation of their data was based on UO_2^{++} ion, however the formula and configuration of uranyl ion in saturated solutions may be considerably different than in dilute solution due to complex ion formation. Further, in the more recent investigation of Satyanarayana three Raman lines were found for uranyl chloride which were not reported by Conn and Wu.

X-ray diffraction studies of a number of crystalline uranyl salts have been performed.[7,8] In $NaUO_2Ac_3$ and UO_2F_2 it was found that a linear

TABLE II. Data and results of Experiments I and II.

	Experiment I	Experiment II
Formula of salt	$UO_2Cl_2 \cdot 3.3H_2O$	$UO_2Cl_2 \cdot 3.0H_2O$
Moles salt added	0.0477	0.104
Moles enriched water added	1.00	1.23
Composition of solution	2.0 *M* uranyl chloride 0.1 *M* HCl	3.0 *M* uranyl chloride 0.65 *M* HCl
Normal O^{16}/O^{18} in water	500	500
Initial O^{16}/O^{18} in enriched water	19.9 ±0.4	22.8 ±0.4
O^{16}/O^{18} in water at various times after dissolving salts		
20 min.	23.4 ±0.4	20 min. 27.8 ±0.5
48 hr.	23.6 ±0.4	60 min. 28.2 ±0.5
		68 hr. 28.0 ±0.5
Calculated O^{16}/O^{18},		
for $r=1.3$	21.2 ±0.4	$r=1.0$ 24.6 ±0.5
for $r=3.3$	23.0 ±0.4	$r=3.0$ 28.4 ±0.5
for complete exchange:	25.0 ±0.4	32.2 ±0.5

O−U−O group existed. The presence of UO_2^{++} ion in uranyl compounds containing more than one oxygen atom per uranium atom was demonstrated in the work of Zachariasen,[9] who studied the x-ray diffraction of some uranates and some of the oxides of hexavalent uranium. In the case of $CaUO_4$, $SrUO_4$, $BaUO_4$, Li_2UO_4, Na_2UO_4, K_2UO_4, UO_3 and U_3O_8 he showed that each uranium atom is surrounded by eight oxygen atoms six of which (OII) lie in a plane with the uranium atom all at a distance greater than the remaining two (OI) which lie above and below the uranium atom on a straight line perpendicular to the plane of the OII oxygen atoms. In calcium uranate the U−OII distance is 2.3±0.3A, while the U−OI distance is 1.91±0.12A. From this work it seems likely that the U−OII bonds are principally of ionic character and crystals of calcium uranate are composed of Ca^{++}, UO_2^{++} and $O^{=}$ ions.

The exchange of oxygen between uranyl ion and water was measured using stable oxygen 18 as a tracer to distinguish directly between these two possible formulas for uranyl ion. The rate of exchange of the oxygen atoms bonded to the uranium atoms should be a function of the type of bonding involved. Thus, the exchange of oxygen would be expected to be very rapid if an ionic bond were involved and relatively slow for a covalent bond. Abundant evidence for this conclusion exists in the slow exchange of covalently bonded atoms where no chemical reaction exists to break the bond involved. Examples of such cases are the exchange of oxygen between water and sulfate ion, perchlorate ion, phenol, methyl alcohol and many others.[10–12] In such cases where a chemical reaction with water exists, as in the carboxylic acids where the rate of exchange is directly related to that of hydrolysis and esterification,[10] the exchange should still be slower

[4] L. V. Coulter, K. S. Pitzer, and W. M. Latimer, J. Am. Chem. Soc. **62**, 2845 (1940).
[5] G. K. T. Conn and C. K. Wu, Trans. Faraday Soc. **34**, 1483 (1938).
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[7] I Fankuchen, Phys. Rev. **43**, 1048 (1933).
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[9] W. H. Zachariasen, Manhattan District Report CC 2870 (1945).
[10] A. Mills, J. Am. Chem. Soc. **62**, 2833 (1940).
[11] E. R. S. Winter, M. Carlton, and H. V. A. Briscoe, J. Chem. Soc. (1940), p. 131.
[12] O. Reitz, Zeits. f. Elektrochemie **45**, 101 (1939).

TABLE III. Experiment III—Data and results.

Formula of heavy salt		$UO_2Cl_2 \cdot 2.28H_2O$
Moles heavy salt added		0.019
Moles normal water added		1.00
Composition of solution		0.8 *M* uranyl chloride 0.8 *M* HCl
Normal O^{16}/O^{18} in water		500
Initial O^{16}/O^{18} in salt (from the ratio of water after 48 hours)		24.6±0.4
O^{16}/O^{18} in water at various times after dissolving heavy salt		
	20 minutes	268±5
	40 minutes	244±5*
	130 minutes	268±5
	18 hours	270±5
	68 hours	278±5
Calculated O^{16}/O^{18}		
	for $r=0.28$	474±9
	for $r=2.28$	276±5
	for complete exchange	192±4

* This low value presumably is due to the use of glassware that had previously contained highly enriched water.

than that expected for a completely ionic bonded oxygen atom. If the rate of exchange of oxygen between uranyl ion and water is measured, the number of each type of uranium oxygen bonds should be revealed.

EXPERIMENTAL

In general the method consisted of preparing a pure uranyl salt hydrate, $UO_2Cl_2 \cdot 3H_2O$, a weighed portion of which was added to a known amount of water. Either the salt or the water was enriched in oxygen 18. Water was distilled from the solution and the isotopic ratio was determined with the aid of a mass spectrometer.

The uranyl chloride was prepared from iron free UCl_3 which was oxidized by hydrogen peroxide in dilute HCl solution to the plus six state. The hydrogen peroxide was decomposed by heating, and uranyl chloride was crystallized from the solution. After filtering, the salt was dried by pumping for several hours on a vacuum line and stored over magnesium sulfate. The crystalline salt was markedly hygroscopic, for if it was allowed to stand in the atmosphere a viscous solution resulted. It was possible, however, to determine the molecular weight by rapidly weighing a sample and igniting it to U_3O_8. The ratio of chlorine to uranium was determined by igniting a sample to U_3O_8 and simultaneously collecting the chlorine evolved in hydrogen peroxide. The chloride was then analyzed by the standard micro determination of chloride. This involved the destruction of hydrogen peroxide by heating, buffering the solution and titrating with standardized silver nitrate solution using dichlorfluorescein as an adsorption indicator. Various samples of uranyl chloride had different compositions, depending on the time of dessication. The accuracy in the molecular weight and in the U/Cl ratio was ±0.1 percent. The oxygen was determined by difference assuming a formula of the type $UO_2Cl_2 \cdot xH_2O$.

All of the exchange measurements were performed at room temperature. In order to obtain a significant measure of the isotopic composition of the water it was necessary to separate the water from the solution within a time that was short compared to the half time of the exchange reaction. This was accomplished by vacuum molecular distillation. Five to ten ml of the solution to be measured were placed in the still under a positive pressure of dry nitrogen gas to keep water vapor from the air out of the apparatus. The condensing finger was filled with liquid nitrogen, the still evacuated and the water collected as ice. The sample in the still was cooled by its own evaporation to a solid below 0°C within two minutes of the time that the distillation was begun. It was assumed that this would quench any exchange reaction having a measurable rate at room temperature. When ice equivalent to several ml of water was collected, the liquid nitrogen was allowed to evaporate, the pumping stopped and hot water was poured into the collecting finger. The ice then melted and was collected in a separate vessel.

The mass spectrometer used in this work was essentially a Nier type[13] constructed by the author. It could not be baked free of water vapor in a reasonable time so it was necessary to measure the isotopic composition of the water by the method of Cohn and Urey.[14] This consisted of equilibrating 3 to 5 ml of water with 50 ml of dry carbon dioxide gas by shaking them together for five hours. The CO_2 was analyzed in the mass spectrometer and the O^{16}/O^{18} ratio in the water calculated from the result. Although the accuracy of the mass analysis appeared to be within 1 percent, the reproducibility was more nearly ±2 percent. Consequently, this accuracy is believed to represent the actual uncertainty in the results. The correction for dilution of the water by CO_2 was made in the calculation, however, it amounted to but 2 to 3 percent change in the ratio.

CALCULATIONS

All of the experiments were similar in nature. They consisted of adding a known weight of uranyl chloride to a known amount of water either of which is enriched in oxygen 18, and measuring the isotopic ratio of the water at various time intervals after dissolving the salt. The calculated values of the ratio O^{16}/O^{18} were obtained by the following considerations. The number of moles of O^{16} and O^{18} in the water and uranyl chloride are shown in Table I.

The value of R or the ratio O^{16}/O^{18} of the water after mixing may be expressed in terms of known or measurable quantities by inspection of Table I. At equilibrium, i.e. complete exchange, the isotopic ratio of the water is given by the following ex-

[13] A. O. Nier, Rev. Sci. Inst. 11, 212 (1940).
[14] M. Cohn and H. C. Urey, J. Am. Chem. Soc. 60, 679 (1938).

pression:

$$R=[pN_1^{16}+(q+2)sN_2^{16}/pN_1^{18}+(q+2)sN_2^{18}].$$

If r of the q oxygen atoms exchange or become indistinquishable from water, the expression becomes,

$$R=[pN_1^{16}+rsN_2^{16}/pN_1^{18}+rsN_2^{18}].$$

DATA AND RESULTS

The first experiment performed was 0.1 N in HCl, the acid being due to some residual acid in the uranyl chloride. The acid concentration was determined by dissolving a weighed sample of uranyl chloride in distilled water and adding a saturated solution of potassium iodate until all the uranium was precipitated as uranyl iodate. The precipitate was filtered and washed. Then the supernatant solution was titrated with standardized sodium hydroxide and the acid concentration calculated from the result. In the second experiment the water was made 1.0 N in HCl before dissolving the salt. The data obtained are shown in Table II. The composition of the solution was determined by measuring the volume upon mixing the components of the solution in a separate experiment.

In order to clarify the results of the first experiments a third experiment was performed. It consisted of repeating experiment 1 mixing normal uranyl chloride with water enriched in oxygen 18 and allowing the solution to stand for 48 hours. At that time some water was removed from the solution and its isotopic ratio was determined. Within experimental error the results of experiment 1 were duplicated. From this solution uranyl chloride was recrystallized, dried and analyzed as $UO_2Cl_2 \cdot 2.28H_2O$. It was assumed that all of the oxygen in the recrystallized uranyl chloride was of the same isotopic composition as the water from which it was recrystallized except for those oxygen atoms which did not exchange during the 48 hour standing period and the subsequent recrystallization period of about 24 hours. A weighed portion of this heavy uranyl chloride was then dissolved in ordinary 1 N HCl and the isotopic ratio of the water in this solution was measured after various time intervals. The data obtained are shown in Table III.

DISCUSSION OF EXCHANGE MEASUREMENTS

Since complete exchange did not occur in any of the experiments, it is evident that the species of uranyl ion formed do not exchange rapidly with water. Because of the stoichiometry involved it may be seen that all but two oxygen atoms per uranium atom exchange or become indistinguishable from the water. Therefore, considering the first two experiments, regardless of the exact configuration of oxygen and uranium atoms in solid uranyl chloride,

TABLE IV. Raman measurements of uranyl salts.

Solution	cm^{-1}* Assignment	Author
Uranyl Chloride saturated solution	860(s) symmetric stretching 210(s) deformational bending	Conn and Wu Conn and Wu
Uranyl Chloride saturated solution	865(s)(p) 853(w) 226(m) 197(m) 909(w) asymmetric	Satyanarayana Satyanarayana Satyanarayana Satyanarayana Satyanarayana
Uranyl Chloride 1.2M, 1.2M NH_4Cl 1.0M HCl	864(s) 204(m)(d)	Crandall Crandall
Uranyl Sulfate saturated solution	860(s) 210(s)	Conn and Wu Conn and Wu
Uranyl Nitrate saturated solution	863(d) 210(s)	Conn and Wu Conn and Wu
Uranyl Perchlorate saturated solution	880(s) 199(w)(d)	Crandall Crandall

* (s) strong, (m) medium, (w) weak, (d) diffuse, (p) polarized.

the most likely formula of the stable uranyl ion formed upon solution of uranyl chloride in water is UO_2^{++}, disregarding any complexing by chloride ion. In experiment III, assuming from the results of the first two experiments that the stable ion is UO_2^{++}, all of the heavy oxygen that was in the recrystallized salt from the first part of the experiment, i.e., the oxygen in the water of crystallization, exchanged with the normal water in the second part. Thus, the logical interpretation of this result is that the UO_2^{++} ion was unchanged throughout the entire process of dissolving uranyl chloride in dilute acid, recrystallizing and redissolving in dilute acid. The ion $U(OH)_4^{++}$ with equivalent oxygen atoms cannot be an important species in the solutions studied. Of course an ion with four oxygen atoms bonded to the uranium atom where two oxygen atoms are bonded much more weakly than the other two is not excluded on the basis of these measurements.

Although it has been established that UO_2^{++} is the formula of uranyl ion in solution, there remains the possibility that the uranium atom is covalently bonded to more than two oxygen atoms in solid uranyl chloride. However, when UO_2^{++} ion forms a crystal it would have to pick up water to form a covalently bonded group containing more than two oxygen atoms. Since these oxygen atoms would be equivalently bonded to the uranium atom, their isotopic ratio would not be the same as either the oxygen atoms of UO_2^{++} ion in solution or of the water from which it was crystallized. Consequently, the result expected for the case of a covalent unit containing more than two equivalent oxygen atoms per uranium atom in uranyl chloride dissolving to form UO_2^{++} ion is not in agreement with experiment. This conclusion is in agreement with that of Zachariasen[9] for other uranyl salts.

From these exchange measurements it may be concluded that UO_2^{++} is covalently bonded in dilute HCl solution as well as in solid uranyl

chloride. The formula of uranyl ion in dilute HCl solution is UO_2^{++} rather than $U(OH)_4^{++}$, neglecting complexing by the anions present, unless the $U(OH)_4^{++}$ ion has two uranium oxygen bonds which are much weaker than the other two. From the entropy considerations of Coulter, Pitzer, and Latimer, it is evident that UO_2^{++} ion attracts water with stronger or more specific forces than other large dipositive ions. This might arise from hydrogen bonding, or ion-dipole bonding of the oxygen of the water to the uranium, or by a combination of both.

DISCUSSION OF RAMAN DATA

As mentioned previously the Raman spectra of solutions of uranyl salts have been measured.[5,6] These spectra have been interpreted on the basis of the selection rules for the gaseous UO_2^{++} ion. The data are compiled in Table IV along with some unpublished results obtained by the author. These results were obtained using the same equipment as Gwinn and Neu.[15] The 5461A line of mercury was used for the excitation.

The configuration assigned to uranyl ion from the Raman results is a bent structure. This may be contrasted with the linear configuration established for UO_2^{++} in several uranyl salts by Zachareisen and others.[7–9] Due to the lack of complete experimental agreement between the various authors and to the lack of assignment of the extra lines found by Satyanarayana, this evidence alone cannot be used as positive proof of the formula of uranyl ion as far as the number of oxygen atoms in the ion are concerned. A plausible interpretation of the Raman data may be stated, if the effects of complex ion formation are considered.

All of the Raman spectra have been obtained using concentrated solutions of the salts in which uranyl ion is complexed by the anion present to a large extent possibly except in the case of the perchlorate. The ionic bonds between the uranium atom and the complexing anions would not be expected to give rise to observable Raman spectra. They would, however, be expected to shift the vibration frequencies of the uncomplexed ion to some degree. This complexing may also change the configuration of uranyl ion from a linear to a bent form, or be a major factor in breaking down the selection rules for the gaseous ion. There is a real difference in the frequency of the symmetric stretching vibration of uranyl perchlorate 880 cm^{-1}, where presumably little or no anion complexing exists, and 865 cm^{-1}, 864 cm^{-1} and 860 cm^{-1} reported for uranyl chloride, 860 cm^{-1}, for uranyl sulfate and 863 cm^{-1} for uranyl nitrate. This difference of 15 to 20 cm^{-1} probably represents the frequency shift due to complex ion formation.

It may be noted in the results of Satyanarayana for uranyl chloride that the first four lines listed may be considered as two doublets the average frequencies of which lie close to 860 cm^{-1} and 210 cm^{-1} as reported in the other investigations. These doublets may be due to two different complex ions present in saturated uranyl chloride, one of which is much less abundant than the other. The lines due to the complex ion of lower concentration may have been missed by Conn and Wu as well as this author, for in neither study was the weak line at 909 cm^{-1} reported. This line, found by Satyanarayana, is presumably due to the major complex ion in saturated uranyl chloride.

Whether the configuration of uranyl ion is linear or bent cannot be determined due to the uncertainty in extrapolating the selection rules for the gaseous ion to the concentrated solutions studied. However, the Raman data are in agreement with the formula of uranyl ion, UO_2^{++}, if the effects of anion complexing are considered.

ACKNOWLEDGMENTS

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Motions of Molecules in Condensed Systems: V. Classification of Motions and Selection Rules for Spectra According to Space Symmetry

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A classification of the motions of a crystal is made on the basis of space symmetry, with the aid of the Born-Karman boundary conditions. It is shown that the selection rules for fundamentals arising from this classification are the same as those derived by the unit cell analysis of Bhagavantam and Venkatarayudu. A relation between the unit cell and site analyses is investigated which makes it possible to obtain the unit cell results by means of the usually simpler site method. A space symmetry criterion for the appearance of composite transitions is established, and some of the effects expected on the basis of this criterion are discussed. The character tables for space groups are described.

INTRODUCTION

PROCEDURES for determining the selection rules for optical transitions in crystals have been devised by Bhagavantam and Venkatarayudu,[1] and also by Halford.[2] In the first of these, the motions of the crystallographic unit cell are considered, and in the other attention is focussed upon the motions of individual molecules within the crystal. It is shown in this communication that both of these methods may be derived from a treatment which considers the motions of a crystal segment composed of an arbitrary number of unit cells and subject to the Born-Karman boundary conditions. Besides providing a justification for the application of these methods, this treatment also clarifies the relation between them.

These results are obtained by the use of a variety of groups, all of them related to the space group which describes the symmetry of the crystal under investigation. It is convenient before proceeding further to collect together the definitions of these groups.

SOME RELATED GROUPS

Space Group[3]

If a crystal were infinite in extent, it would admit an infinite number of symmetry operations, including translations, proper and improper rotations, and combinations of these. There are a limited number of ways of combining such operations to form groups, and the symmetry of a crystal may be described by giving that one of this limited number of space groups which contains as its elements the symmetry operations of the crystal.

Finite Space Group

In our applications of group theory to crystals, we shall find it convenient to deal with finite rather than infinite groups. The fundamental reason for using a finite group is that we are then able to employ results from the well-known and relatively simple theory of representations of finite groups. In addition, physical crystals are actually finite, and it seems to us more consistent to describe their symmetry in terms of groups containing finite, rather than infinite, numbers of symmetry operations. The finite groups in question are related to the space groups and we define them in the following paragraph.

Let $\mathbf{t}_1$, $\mathbf{t}_2$, and $\mathbf{t}_3$ be the fundamental lattice vectors defining the primitive unit cell of the crystal; N_1, N_2, and N_3 be fixed positive integers; and n_1, n_2, and n_3 be any integers. Then, those elements of the infinite space group which differ in their effect only by a translation of

$$n_1N_1\mathbf{t}_1+n_2N_2\mathbf{t}_2+n_3N_3\mathbf{t}_3$$

are considered to be the same element of the finite space group. The group so defined is really a group of the symmetry operations of lattices with lattice constants $N_1\mathbf{t}_1$, $N_2\mathbf{t}_2$, and $N_3\mathbf{t}_3$. Translations by these vectors and sums of them carry a lattice into itself and so are equivalent to the identity.

Use of the finite space group in analyzing the motions of the crystal is equivalent to adopting the Born-Karman cyclic boundary conditions.[4] If we are considering the motions of the atoms contained in a block of crystal with edges $N_1\mathbf{t}_1$, $N_2\mathbf{t}_2$, and $N_3\mathbf{t}_3$, these conditions require that we calculate the normal modes of the crystal as if it extended to infinity, but with the restriction that those atoms which are separated from each other by vectors

$$n_1N_1\mathbf{t}_1+n_2N_2\mathbf{t}_2+n_3N_3\mathbf{t}_3$$

have the same displacements. The motions be-

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[2] R. S. Halford, J. Chem. Phys. **14**, 8 (1946). The pattern of this symmetry argument was first used by H. Bethe, Ann. d. Phys. **3**, 133 (1929).

[3] W. H. Zachariasen, *Theory of X-Ray Diffraction in Crystals* (John Wiley and Sons, Inc., New York, 1945), Chapters I and II. This reference contains a modern account of space group theory.

[4] M. Born, Proc. Phys. Soc. London **54**, 362 (1942). This reference reviews the arguments for the validity of the cyclic boundary condition.

TABLE I. Group orders.

Group	Order
Infinite space	Infinite
Finite space	$N_1N_2N_3H$
Finite translation	$N_1N_2N_3$
Factor	H
Site*	H/n

* n is equal to the number of equivalent sites in a set.

longing to irreducible representations of the finite space group will have this property.

Translation Group

It is shown in the standard works on space group theory that any space group may be regarded as a product of an invariant subgroup, consisting of the elements corresponding to pure translations, and a factor group. This property is shared by the finite space group, the only difference being that its invariant subgroup is itself finite. It may be derived from the translation subgroup of the corresponding infinite space group by the same process of contraction described above. Both finite and infinite translation groups are Abelian.

Factor Group

The cosets of the translation group in the space group are found to form a group themselves. This factor group is the same for corresponding infinite and finite space groups. The factor groups are always isomorphous with one of the thirty-two crystallographic point groups, although some of them may involve cosets containing other than purely point operations combined with lattice translations, i.e., screw rotations or glide reflections.

Site Group

A site is defined as a point which is left invariant by some operations of the space group. These operations may be shown to form a group which we will call the site group. Every point is thus a site, having at least the trivial site group C_1. A site group is necessarily isomorphous with some subgroup of the factor group, and, of course, involves only point symmetry operations, for no glide reflection or screw rotation can leave any point invariant. It must be emphasized that the site group contains *all* elements which leave the site invariant.

The various procedures for determining selection rules in crystals may be more precisely described by stating the kind of group used in the analysis of the motions. The present method analyzes the motions of a parallelopiped shaped crystal according to the finite space group; Bhagavantam and Venkatarayudu analyze the motions of the unit cell under the factor group; and Halford analyzes the motions of a molecular unit in the crystal according to the group of its site. In each case the analysis follows the pattern long familiar in the treatment of gaseous molecules. The representation of the motions of the system is first determined and then reduced among the irreducible representations of the symmetry group of the system. Knowledge of the number of motions belonging to each irreducible representation leads immediately to the number of motions active in each spectrum; further manipulation of this information gives a classification of overtone and combination bands.

In order to follow this pattern, we must have information about the forms of the irreducible representations of the finite space groups, the factor groups, the site groups, and also of the translation groups. Since the connections between the various analyses depend upon relationships between the representations of the various groups, such relationships are also examined here.

RELATIONS AMONG THE GROUPS AND THEIR REPRESENTATIONS

Relations Among Group Orders

The relations among the group orders set forth in Table I are deduced quite simply. The order of the finite translation group is the number of distinct translations possible, and this is $N_1N_2N_3$. The order of the product of an invariant subgroup and a factor group is the product of their orders; thus the order of the finite space group is $N_1N_2N_3H$.

The relation between the orders of the site group and factor group is only slightly more difficult to prove. A general point in the unit cell (one not on any symmetry elements) will be carried into $H-1$ other equivalent points by the operations of the factor group. Let us suppose, however, that the point is located on a site with a group of order h. If the factor group is now expanded in cosets of the site group, it is not difficult to see that all the elements of any one coset will have the same effect on the site. There will thus be no more points in the unit cell equivalent to a site than there are cosets of the site group, or H/h, including the site itself. There will be no less than H/h equivalent points, because this would imply that some operation of the factor group not contained in the site group leaves the site invariant. As we have previously pointed out, the site group must contain *all* operations which leave the site invariant. Therefore, if a site has a group of order h, it is one of H/h sites equivalent in the sense that each of them is transformed into the others by those elements of the factor group not contained in the site group. Such equivalent sites have, of course, isomorphous site groups, although the n site groups are not necessarily composed of the same elements of the factor group.

Representations of the Translation Groups

Seitz[5] has shown that representations of the infinite translation group may be set up in the following way. Consider the quantities

$$\exp\{2\pi i \boldsymbol{\kappa}\cdot\mathbf{t}\}$$

where $\mathbf{t}$ is a translation vector of the group and $\boldsymbol{\kappa}$ is a vector of the form

$$\frac{l_1}{L_1}\mathbf{b}_1+\frac{l_2}{L_2}\mathbf{b}_2+\frac{l_3}{L_3}\mathbf{b}_3.$$

Here the l_i are running integers, the L_i are fixed integers, and the $\mathbf{b}_i$ are the vector set reciprocal to the fundamental lattice vectors, $\mathbf{t}_i$. The set of these exponentials with a single value of $\boldsymbol{\kappa}$ forms a representation of the infinite translation group as we run through all values of $\mathbf{t}$. Moreover, if we identify the L_i with the N_i we have previously introduced to fix the finite space group, all the $N_1N_2N_3$ different representations formed by allowing the l_i to assume any integral values are satisfactory representations of the finite translation group. Being one-dimensional, these representations are irreducible. Because an Abelian group has only as many different irreducible representations as it has elements, these representations constitute all the irreducible representations of the finite translation group.

Space Group and Factor Group Representations

We wish to call attention here to differences in the definitions by various authors of the direct product of two groups. For example, Zachariasen[6] defines the direct product of two groups F and G as existing if all the products formed by taking an element of F on the left and of G on the right are included among and include all products formed in the opposite way. Wigner[7] and others adopt the more restrictive requirement that these products be individually commutative; that is, $fg=gf$ for any elements of F and G. The finite space groups are direct products of the finite translation groups and the factor groups in Zachariasen's sense, but generally not in Wigner's. Therefore, we may not employ the rather simple procedures for setting up the irreducible representations of the finite space group which would apply if it were a Wigner direct product.[7] To confuse the situation still more, there is the concept of the direct product of two representations of the same group, something different from either the Zachariasen or Wigner direct products.

Seitz[5] has shown how the matrices of the true irreducible representations of the space groups may be found. We shall not require such complete information about the space group representations at this point, although when it is needed later it will be obtained by Seitz' methods. Certain special irreducible representations of the finite space group are very quickly gotten, however, and these are the ones of greater momentary interest to us, because, as we shall show, they contain all modes which are active as fundamentals in either infra-red spectrum or Raman effect. These representations are obtained, each from a different irreducible representation of the factor group, by merely assigning to each element of the space group the matrix which corresponds to its coset considered as an element of the factor group. It is readily seen that these are irreducible representations of the finite space group, which we shall call the factor group representations, and are equal in number and identical in dimensionality with the irreducible representations of the factor group. One factor group representation of the finite space group is obtained from each irreducible representation of the factor group. Because all allowed factor groups of space groups are isomorphous with crystallographic point groups and so have the same well-known character tables, we are in a position to write down immediately that part of the character table of the finite space group which corresponds to factor group representations.

Factor Group and Site Group Representations

As we have pointed out above, a site group is isomorphous with a subgroup of the factor group. If we select from the matrices of an irreducible representation of a group those corresponding to the elements of a subgroup, they must constitute a representation, not necessarily irreducible, of the subgroup. It is convenient to express this fact in terms of an equation in the characters of the irreducible representations of the group and subgroup, in this case the factor group and the site group.

$$\chi_i^{f\cdot g\cdot}(R)=\sum_j a_{ij}\chi_j^{s\cdot g\cdot}(R). \tag{1}$$

R is an element of the site group S, $\chi_i^{f\cdot g\cdot}(R)$ is the character of R in the i'th irreducible representation of the factor group F, $\chi_j^{s\cdot g\cdot}(R)$ is the character of R in the j'th irreducible representation of the site group S, and the a_{ij} are coefficients depending on the groups F and S and the representations i and j, but not on R.

By the usual group theoretical equation we have

$$a_{ij}=(1/h)\sum_{R\text{ in }S}\chi_j^{s\cdot g\cdot *}(R)\chi_i^{f\cdot g\cdot}(R). \tag{2}$$

However, the a_{ij} can usually be determined by inspection of the character tables of S and of the point

[5] F. Seitz, Ann. Math. **37**, 17 (1936).
[6] Reference 3, p. 248.
[7] E. Wigner, *Gruppentheorie* (Edwards Bros., Ann Arbor, 1944), Chapter XVI.

group isomorphous with F. Tables which aid in the determination of the a_{ij} are given by Herzberg.[8]

We have in this section presented the purely group-theoretical considerations which are necessary for the interpretation of the gross features of crystalline spectra. In the succeeding sections we shall show how the group-theoretical ideas are applied.

CLASSIFICATION OF THE MOTIONS OF A CRYSTAL

As in the case of molecules, the next step after determining the symmetry group exemplified by the system is to find out how the representation of the motions of the system is reduced among the irreducible representations of this group. This procedure is carried out as usual by means of the characters of the representation of the motions.

We may expect that the analysis under the finite translation group, a subgroup of the finite space group, will provide us with a less detailed classification than the analysis under the finite space group itself. Nevertheless, the simpler translation group classification is valuable in itself and also as an aid in interpreting the space group results. In a similar way, the site group analysis is useful not only in itself but also in obtaining and interpreting the factor group predictions.

Finite Translation Group

We shall employ a block of crystal with edges $N_1\mathbf{t}_1$, $N_2\mathbf{t}_2$, and $N_3\mathbf{t}_3$ as the dynamical system for the finite translation and space groups. This block contains $N_1N_2N_3$ primitive unit cells.

The only operation of the finite translation group which leaves points invariant is the identity. If there are m atoms in the unit cell, the character system of the motions is

$$\begin{aligned} \chi_M(E) &= 3mN_1N_2N_3, \\ \chi_M(\mathbf{t}) &= 0. \quad (\mathbf{t} \neq E) \end{aligned} \tag{3}$$

The number of motions falling in the representation given by the vector $\boldsymbol{\kappa}$ is

$$\begin{aligned} n_{\boldsymbol{\kappa}} &= (1/N_1N_2N_3) \sum_{\mathbf{t}} \chi_{\boldsymbol{\kappa}}(\mathbf{t})\chi_M(\mathbf{t}) \\ &= (1/N_1N_2N_3)N_1N_2N_3 \times 3m \times 1 \\ &= 3m. \end{aligned} \tag{4}$$

Thus each representation of the finite translation group contains $3m$ motions of the crystal. This corresponds to the well-known result that the equations of motion of a three-dimensional crystal with Hooke's Law forces may be reduced to sets of determinantal equations of degree $3m$. Our result is more general than this, however, for it does not depend upon the assumption of harmonic forces.

If we do assume harmonic interactions, the vibrational eigenfunction of the crystal may be written as a product of one-dimensional oscillator functions, each depending on only one normal coordinate. Each one-dimensional function must belong to an irreducible representation of the translation group, and the representation of the product function will be the direct product of the representations of the one-dimensional functions. If the one-dimensional function of a normal coordinate i which belongs to the $\boldsymbol{\kappa}_i$ representation is in its p_i-th level, its translation group representation is that characterized by the vector $p_i\boldsymbol{\kappa}_i$. It may be seen, as a result of the formula for the characters of the direct product and the particular form of the translation group irreducible representations, that the vector characterizing the representation of the state of the whole crystal when the functions of the coordinates i are in their p_i-th levels is just $\sum_i p_i\boldsymbol{\kappa}_i$.

Finite Space Group

We shall discuss here the reduction of the representation of the motions among only those irreducible representations of the finite space group which are derived from the factor group's representations, since these turn out to be the ones of chief physical interest. For convenience, let v(coset) be defined as follows. We apply in turn all of the operations of a coset (of the finite translation group in the finite space group) to the crystal, and watch any one particular unit cell. Each time an atom is left invariant in this unit cell we count one, and the sum of our counts is v(coset). v(coset) is of course independent of the particular unit cell which is used in the counting. It is now easy to write an expression for the sum of the characters of the motions over all elements of one coset. The contribution of any one unit cell to this sum is

$$v(\text{coset})(\pm 1 + 2\cos\varphi(\text{coset})).$$

Since there are $N_1N_2N_3$ unit cells in all, we have

$$\begin{aligned} &\sum_{R \text{ in coset}} \chi_M(R) \\ &\quad = N_1N_2N_3 v(\text{coset})(\pm 1 + 2\cos\varphi(\text{coset})). \end{aligned} \tag{5}$$

φ(coset) is the angle of rotation associated with the coset.

The representations of the finite space group derived from the factor group have the property that all elements of a coset have the same character in them. The number of times one of these factor group representations appears in the representation

[8] G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), p. 237.

of the motions of the crystal is

$$n_i^{f.g.} = (1/N_1N_2N_3H) \sum_{R \text{ in sp.g.}} \chi_i^{f.g.*}(R)\chi_M(R)$$
$$= (1/N_1N_2N_3H) \sum_{\text{cosets}} (\chi_i^{f.g.*}(\text{coset}) \times \sum_{R \text{ in coset}} \chi_M(R))$$
$$= N_1N_2N_3(1/N_1N_2N_3H) \sum_{\text{cosets}} \chi_i^{f.g.*}(\text{coset}) \times v(\text{coset})(\pm 1 + 2\cos\varphi(\text{coset})) \quad (6)$$

$$n_i^{f.g.} = (1/H) \sum_{\text{cosets}} \chi_i^{f.g.*}(\text{coset}) \times v(\text{coset})(\pm 1 + 2\cos\varphi(\text{coset})).$$

We have reduced the calculation of the number of motions in a factor group representation of the space group to a summation over H cosets which involves, besides the quantity v(coset) dependent on the particular arrangement of atoms in the crystal, only well-known quantities tabulated in the character tables of crystallographic point groups.

Factor Group

The quantities v(coset) may also be determined in a slightly different manner. Consider one unit cell and one element from each coset. An atom will contribute *one* to v(coset) if the one element from the coset either leaves the atom in its initial position or carries it to a point in another unit cell which has the same coordinates relative to the cell corner. Otherwise the atom contributes *zero*. This procedure gives the same values for v(coset) as our earlier definition because if one operation of a coset carries an atom into the same relative location in another unit cell, there must exist another operation belonging to the same coset which leaves the position of the atom unchanged.

With this definition of v(coset), we have exactly the method of Bhagavantam and Venkatarayudu.[1] Their procedure is equivalent to choosing our N_i all equal to unity, for they consider just one unit cell and its transformations under representative operations of the factor group. In this case, the finite space group is isomorphous with the factor group and the factor group representations constitute all the representations. The present treatment has independently justified the Bhagavantam and Venkatarayudu method and has furthermore shown that it gives the correct population of the factor group representations *whatever the values* of N_i.

Site Group

There are no complications in carrying out the classification for the site group. The occupant of the site is treated just as if it were an independent molecule having the symmetry of the site.[2] Another section of this communication deals with means of determining the results of Bhagavantam and Venkatarayudu method through a preliminary site analysis.

SELECTION RULES

The usual formulation of the selection rules for optical transitions is employed. An infra-red transition is permitted if the representation of $\psi^*_{\text{initial}}\psi_{\text{final}}$ contains a representation of a vector. A Raman transition may occur if a representation of a symmetric tensor is to be found in the representation of $\psi_i^*\psi_f$. Certain directional properties may be deduced from these rules; if, for example, only the representation of the z component of a vector appears in that of $\psi_i^*\psi_f$, then only light polarized in the z direction can effect the transition from state i to state f.

We shall investigate the selection rules according to the finite translation group, the finite space group, the factor group, and the site group. It is to be expected that the finite space group selection rules will be the most restrictive and will include the rules derived for the other cases. There are, however, a number of reasons for considering the other groups. Since we have not yet explicitly worked with the Seitz representations of the space group, we shall handle the problem of combinations and differences approximately at first, with the aid of the translation group. The analysis for fundamentals under the space group will be seen to be formally identical with that under the factor group. And finally, a site analysis not only leads to the factor group results, as we shall show, but also provides physically important information about splittings of molecular frequencies due to coupling in the crystal.

Activity Representations

We may call those irreducible representations which occur in the representations of vectors and symmetric tensors the activity representations. They may be determined from the usual equations for the characters of these representations.

$$\left.\begin{aligned} \chi_{\text{Vector}}(R) &= \pm 1 + 2\cos\varphi(R) \\ \chi_{\text{Sym. Tensor}}(R) &= 2 \pm 2\cos\varphi(R) + 2\cos 2\varphi(R) \end{aligned}\right\}. \quad (7)$$

With the aid of these formulas it is easy to pick out the activity representations of the various groups we are employing. The finite translation group has just one activity representation, the totally symmetric one ($\kappa = 0$). The activity representations of the finite space group may be obtained by noting that only those functions which belong to the factor group representations of the finite space group also belong to the totally symmetric representation of the finite translation group. As we have pointed out a few lines above, vectors and symmetric tensors are invariant under translation and so belong to the

totally symmetric translation group representation. They must therefore belong to factor group representations in the space group, and it is not difficult, using the relations in Eq. (7), to show that the representations to which they do belong correspond to the activity representations of the factor group. This justifies our momentary disregard for all but the factor group representations, for no other representations of the space group can contain active fundamentals. Both factor group and site group activity representations may be readily obtained from the character tables for these groups.

Selection Rules for Fundamentals

Analysis according to any of the groups we are considering gives us a more or less refined selection rule for fundamentals. The general rule is, of course, that a vibration is infra-red or Raman active in its fundamental if the corresponding normal coordinate belongs to one or another of the activity representations. As we have shown, the one activity representation of the finite translation group contains $3m$ motions, from which we must subtract 3 for translations of the whole crystal. We need not worry about rotations because rotations of the whole crystal are not admissible motions under the Born-Karman boundary conditions. We may conclude that under the finite translation group at most $3m-3$ fundamentals may appear in either spectrum, where m, we recall, is the number of atoms in one unit cell of the smallest possible volume (not necessarily the conventional crystallographic unit cell, which may include several of ours).

The analysis for fundamentals under the finite space group and under the factor group is formally the same, as may be seen from the discussion of the Bhagavantam and Venkatarayudu method above. The result is to cut down the number of spectroscopically active fundamentals from $3m-3$ to the number of motions belonging to the appropriate factor group activity representations. The whole procedure may be carried out according to the directions of Bhagavantam and Venkatarayudu, or else by an alternative and usually simpler method depending on the site analysis, which will be described in the next section.

RELATIONS BETWEEN FACTOR GROUP AND SITE GROUP ANALYSES**

We present here some connections between the results of the site group analysis of Halford and the factor group analysis of Bhagavantam and Venkatarayudu. As we have shown, Eq. (6) holds true for the populations of the factor group representations even if a finite space group with arbitrary N_i is employed. This equation may be written in such a way as to show more clearly the connection with the site analysis. Let the character of the operation R in the representation of the motions of the unit cell as obtained by Bhagavantam and Venkatarayudu, $\Xi_M(R)=v(R)(\pm 1+2\cos\varphi)$, be broken up into a sum of contributions $\Xi_M{}^{\text{site}}(R)$ from each site. (We here consider a set of n equivalent sites; in general a summation over the different sets is also required.) We obtain

$$n_i{}^{\text{f.g.}}=\frac{1}{H}\sum_{\text{sites}}\sum_{R\text{ in f.g.}}\Xi_M{}^{\text{site}}(R)\chi_i{}^{\text{f.g.}*}(R). \quad (8)$$

For any one site, $\Xi_M{}^{\text{site}}(R)$ is zero for all elements not in the site group, and

$$\chi_i{}^{\text{f.g.}}(R)=\sum_j a_{ij}\chi_j{}^{\text{s.g.}}(R). \quad (1)$$

The contribution of one site to the sum is

$$\sum_j\sum_{R\text{ in s.g.}} a_{ij}\chi_j{}^{\text{s.g.}*}(R)\Xi_M{}^{\text{site}}(R). \quad (9)$$

Now, $\Xi_M{}^{\text{site}}(R)$ is just the character for the motions of one site occupant, $\chi_m{}^{\text{s.g.}}(R)$, so the contribution of one site to the sum of Eq. (8) may be written

$$\sum_j\sum_{R\text{ in s.g.}} a_{ij}\chi_j{}^{\text{s.g.}*}(R)\chi_m{}^{\text{s.g.}}(R)=h\sum_j a_{ij}n_j{}^{\text{s.g.}} \quad (10)$$

where $n_j{}^{\text{s.g.}}$ is the number of times the j'th irreducible representation of the site group appears in the representation of the motions of the site occupant in the site group. Since all n sites are equivalent, each must make the same numerical contribution to the sum. Making use of the relation

$$H=nh$$

we get

$$n_i{}^{\text{f.g.}}=(nh/H)\sum_j a_{ij}n_j{}^{\text{s.g.}}=\sum_j a_{ij}n_j{}^{\text{s.g.}}. \quad (11)$$

This proof holds whether or not the symmetry elements of the n equivalent sites are parallel.***

** I wish to point out that the contents of this section refute the rather exaggerated ultimate conclusion reached by Mme. Couture [J. Chem. Phys. **15**, 153 (1947)] in her criticism of the site method. On the other hand, Mme. Couture's preliminary remarks, concerned not with the method but with my tables showing the availabilities of sites and with my erroneous analysis of aragonite, are points well taken. It is recommended that any user of my tables who approaches these problems for the first time should consult Mme. Couture's note in order to be forewarned of a difficulty which may be encountered occasionally, most likely in crystals containing more than one species of ion or molecule. I hope that Mme. Couture's views and my own are otherwise not so different as they may have appeared. It has not been my intention to imply that the site method offers anything more than a convenient, and often sufficient, first approximation to crystalline spectra.—R. S. H.

*** It may assist the reader to appreciate the content of Eq. (11) if we remark that it has an application in the prediction of vibrational selection rules for free molecules. The atoms of a molecule may be divided into symmetrically equivalent sets, such that the covering operations of the molecule will transform any one member of a set into the others. Each member of one of these sets occupies a site in our sense, and the

From the relation given in Eq. (1) we have

$$\chi_i^{f.g.}(E)=\sum_j a_{ij}\chi_j^{s.g.}(E). \tag{12}$$

Another connection between the dimensionalities of the representations of the two groups, useful as a check on the a_{ij}, is

$$\sum_i a_{ij}\chi_i^{f.g.}(E)=n\chi_j^{s.g.}(E). \tag{13}$$

There are $\chi_j^{s.g.}(E)n_j^{s.g.}$ motions corresponding to the representation j of the site group. Since there are n sites, there must be $n\chi_j^{s.g.}(E)n_j^{s.g.}$ motions corresponding to representation j of the site group in the unit cell. Another expression for this last quantity is

$$\sum_i a_{ij}\chi_i^{f.g.}(E)n_j^{s.g.}.$$

The approach that we recommend to the interpretation of the spectrum of a crystal is to carry out first a site analysis (which often does not require a map of the unit cell). This will yield an adequate interpretation for the grosser, if not all, the details of the spectrum. If finer details remain to be explained, resort may then be had to the unit cell analysis, using the known a_{ij} to compute $n_i^{f.g.}$ from the already determined $n_j^{s.g.}$. This scheme precludes any errors due to choice of too large a unit cell, for the selection of the most primitive cell as the basis of the factor group analysis is automatically assured. In the absence of any other advantage, this procedure gives a better idea of the form of the motions in the unit cell and especially of the connection between molecular modes and crystal modes. Moreover, the second step may often be omitted, especially with the aid of some general deductions set forth in the next paragraph.

On the basis of the foregoing relations, we may make some general statements about the differences between the site analysis and the factor group analysis, differences which correspond essentially to coupling of vibrations between occupants of different sites.

(1) A motion which is a member of a degenerate set under S will still be a member of a degenerate set in F. Since the a_{ij} are integral, a motion cannot go into a representation of F which has smaller dimensionality than its representation in S.

(2) A motion will not be assigned spectral activity in F and inactivity in S, for the characters of the dipole moment and polarizability are the same for the common elements of S and F.

(3) A depolarized motion in S will not become polarized in F, since only the totally symmetric representation of S can contribute to the totally symmetric representation of F.

(4) Motions may become more degenerate in F than in S, they may lose spectral activity, and polarized motions may become depolarized.

(5) Subject to the conclusions stated above, a band or line expected from S may become several times duplicated in F, the number of times not to exceed the number of sites in a unit cell. Such multiplets will usually be recognizable without difficulty and can be temporarily grouped together when assessing the suitability of the site analysis. Sometimes different members of a multiplet will appear in different spectra, causing a slight discrepancy in frequencies.

COMBINATIONS AND DIFFERENCES

The Character Tables of Space Groups

The requirement on the wave functions in order that a transition from state i to state f may take place is that the representation of $\psi_i^*\psi_f$ in the finite space group must contain an activity representation. From the space group representations given by Seitz,[5] we may determine if this condition is satisfied for given states i and f by determining the direct product of the space group representations of ψ_i^* and ψ_f and observing whether it contains activity representations. This procedure gives us all the information available from symmetry about composite transitions.

As a preliminary to this space group analysis, we shall first examine the selection rules for composite transitions according to the translation group. These selection rules, as we shall show, are closely related to the space group rules and are useful in finding the latter.

Only if the representation of $\psi_i^*\psi_f$ in the translation group contains the totally symmetric representation can an optical transition from state i to state f possibly occur. The totally symmetric representation will occur in this direct product if, and only if,

$$\boldsymbol{\kappa}_f-\boldsymbol{\kappa}_i=n_1\mathbf{b}_1+n_2\mathbf{b}_2+n_3\mathbf{b}_3 \tag{14}$$

where the n_i are any integers and the $\mathbf{b}_i$ are the vector set reciprocal to the fundamental lattice vectors. We see that the translation group rules require that the translation group representations of final and initial states must be identical in order that a transition may be permitted.

We shall now employ the theorem that a representation of a subgroup may always be formed from those matrices of a group representation which correspond to the subgroup elements. In this case, a

representation of its motions in the site group is just the representation of a vector (which can be looked up in character tables). The number of motions in any representation i of the molecular group may be found by summing the contributions to N_i from each set of sites, giving $N_i=\sum_j \sum_{\text{sets}} a_{ij}n_j$, where n_j is the number of times the representation j of the site group appears in the representation of a vector.

translation group representation is to be formed from a space group representation. Since we already know all the irreducible representations of the translation group in terms of the vectors κ, it must be possible to assign unambiguously to any space group representation those vectors κ which describe the (not necessarily irreducible) representation of the translation group which may be formed from it.

The considerations of the foregoing paragraph provide us with a criterion for determining if a transition may take place between two states, each of them belonging to a representation of the space group. Since the wave functions must also belong to the representations of the translation group formed from their space group representations, the criterion is that, unless Eq. (14) is satisfied, a transition is forbidden. The κ in Eq. (14) are now to be chosen from among the κ associated with the space group representations in question. Rules equivalent to these have been derived by Seitz,[9] who points out that the intensity associated with any one such transition is likely to be very small, since it would be zero for harmonic interactions, and that an appreciable intensity will result only if a large number of such transitions have very closely the same frequency.

Further development of the space group rules requires a knowledge of the character systems of the space groups. A simple extension of the work of Seitz,[5,10] who has constructed the irreducible representations of space groups, enables us to write for an entry in the character table of a space group

$$\chi_j^{\{\kappa\}}(R, \mathbf{t}+\tau_R) = \sum_{\kappa \text{ in } \{\kappa\}} \exp\{2\pi i \kappa\cdot(\mathbf{t}+\tau_R)\}\chi_j^{\{K\}}(R)\delta_{R\kappa,\kappa}. \quad (15)$$

The notation of Eq. (15) requires a somewhat lengthy explanation. The left-hand member is the character, in a representation of the space group identified by the superscript $\{\kappa\}$ and the subscript j, of the space symmetry operation $(R, \mathbf{t}+\tau_R)$, which consists of a point symmetry operation R, a lattice translation $\mathbf{t}$, and a fractional translation† τ_R, which latter appears or not according to the nature of the space group and the operation R. Each of the vectors κ which define irreducible representations of the translation group belongs to some set $\{\kappa\}$ (a "star" in the terminology of reference 10), which may be formed by applying in turn to a particular κ each of the operations of the point group underlying the space group and collecting together the *different* vectors so generated. The chosen κ will be invariant under one or more point symmetry operations which form a subgroup, $\{K\}$, of the point group, and the other vectors from $\{\kappa\}$ will be invariant under the same or isomorphous subgroups. If k is the order of each of these isomorphous subgroups, $\{\kappa\}$ contains H/k members. Since these subgroups are all isomorphous, irreducible representations of different ones of them can be characterized as *equivalent* or *non-equivalent*. We may therefore speak without ambiguity of the j'th irreducible representation of any of the isomorphous groups; it is the representation equivalent to the j'th irreducible representation of $\{K\}$. The symbol $\chi_j^{\{K\}}(R)$ denotes the character of R in $\gamma^{\{K\}}$, the j'th irreducible representation of $\{K\}$; it is also the character in the j'th irreducible representation of a group isomorphous to $\{K\}$ of the element associated with R by the isomorphism. The Kronecker delta, $\delta_{R\kappa,\kappa}$, shows that the diagonal element of the matrix representing $(R, \mathbf{t}+\tau_R)$ is zero when $R\kappa$ differs from κ, that is, when R is not contained in the group which leaves κ invariant. Recapitulating, a vector κ belongs to a set $\{\kappa\}$, associated uniquely with one or more subgroups isomorphous to the subgroup $\{K\}$; the j'th irreducible representations of these subgroups are *equivalent* to $\gamma_j^{\{K\}}$. An irreducible representation of the space group is completely specified (up to a similarity transformation) by giving the set $\{\kappa\}$ and the $\gamma_j^{\{K\}}$ involved in it. As we shall shortly show, one forms all the non-equivalent irreducible representations of the space group by systematically selecting sets of vectors $\{\kappa\}$, combining each in turn with all of the *non-equivalent* irreducible representations for the associated isomorphous subgroups $\{K\}$, and continuing in this way until the supply of vectors has been exhausted.

We digress momentarily to demonstrate that the character system defined by Eq. (15) is orthogonal and that the representations corresponding to it are irreducible and form a complete set. Since these characters have not previously occurred explicitly in the literature, we hope that these considerations will demonstrate their plausibility for readers who are not familiar with the work of Seitz. We form the sum

$$\sum_R \sum_{\mathbf{t}} \chi_j^{*\{\kappa\}}(R, \mathbf{t}+\tau_R)\chi_k^{\{\lambda\}}(R, \mathbf{t}+\tau_R)$$

using Eq. (15) for the χ's. Summing over $\mathbf{t}$, we get

$$\delta_{\{\kappa\},\{\lambda\}} N_1 N_2 N_3 \sum_R \sum_{\kappa \text{ in } \{\kappa\}} \chi_j^{*\{K\}}(R)\chi_k^{\{K\}}(R)\delta_{R\kappa,\kappa}.$$

The sum over R leads to

$$\delta_{\{\kappa\},\{\lambda\}} N_1 N_2 N_3 k \sum_{\kappa \text{ in } \{\kappa\}} \delta_{jk},$$

[9] R. B. Barnes, R. R. Brattain, and F. Seitz, Phys. Rev. **48**, 582 (1935).

[10] L. P. Bouckaert, R. Smoluchowski, and E. Wigner, Phys. Rev. **50**, 58 (1936).

† Seitz applied his methods explicitly only to space groups not containing glide reflections or screw rotations. However, the matrices set up according to these methods do form valid representations even for space groups involving such elements.

or, since there are H/k vectors in $\{\kappa\}$,

$$\sum_R \sum_t \chi_j^{*\{\kappa\}}(R, \mathbf{t}+\tau_R)\chi_k^{\{\lambda\}}(R, \mathbf{t}+\tau_R) = N_1N_2N_3H\delta_{\{\kappa\},\{\lambda\}}\delta_{jk}. \quad (16)$$

This demonstrates both the orthogonality of the character system and the irreducibility of the representations.

In order to prove that we have all the irreducible representations of the space group, it is sufficient to show that

$$\sum_i \{\chi_i(E)\}^2 = N_1N_2N_3H$$

where the summation is over all the different irreducible representations that we have formed. Any of the vectors κ belongs to a set $\{\kappa\}$ containing H/k vectors. Let us first sum partially over all representations associated with one set $\{\kappa\}$. By Eq. (15), $\chi(E)$ for any of these will be $(H/k)\chi_j^{\{K\}}(E)$. If we now sum its square over the different j, we get $(H/k)^2 \sum_j \{\chi_j^{\{K\}}(E)\}^2$ or H^2/k. The set contains H/k members, so we may say that for each member there is an average contribution to $\sum \chi^2(E)$ of $(H^2/k)/(H/k)$, or H. Each of the $N_1N_2N_3$ different κ contributes this same amount, independent of the size of the set to which it belongs, so that the whole sum is $N_1N_2N_3H$. Therefore, the set of representations formed by running through all sets $\{\kappa\}$ and the associated representations $\gamma_j^{\{K\}}$ contains *all* the nonequivalent representations of the space group.

With this formulation of the character table for the finite space group, we return now to the problem of combinations and differences. For binary transitions we must analyze the characters of direct products formed from pairs of space group irreducible representations. The difficulties of analysis and notation can be substantially reduced if we recall the results of the translation group treatment: an activity representation will be contained in the representation of a direct product only when the representations for initial and final states both involve the same vector κ. (Vectors κ which differ by multiples of $\mathbf{b}_i$ give rise to the same translation group representation.) This assures us that we need not examine direct products involving different sets of vectors, or different subgroups $\{K\}$. The characters for direct product of the pertinent kinds of representations of final and initial states must have the forms

$$\chi_j^{*\{\kappa\}}\chi_l^{\{\lambda\}}(R, \mathbf{t}+\tau_R) = \sum_{\kappa \text{ in } \{\kappa\}} \sum_{\lambda \text{ in } \{\lambda\}} \exp\{2\pi i(\lambda-\kappa)(\mathbf{t}+\tau_R)\} \times \chi_j^{\{K\}}\chi_l^{\{K\}}(R)\delta_{R\kappa,\kappa}\delta_{R\lambda,\lambda}$$

wherein $\{\kappa\}$ and $\{\lambda\}$ stand for the same set of vectors, but j and l may stand for two different irreducible representations of the associated subgroup $\{K\}$.

This direct product representation must be reducible among the irreducible representations of the space group. These must include some of the previously discussed factor group representations, since in this case $\{\kappa_f\} = \{\kappa_i\}$. If we denote by $a_i^{f.g.}$ the number of times the ith factor group representation appears in the direct product representation, we find in the usual way

$$a_i^{f.g.} = (1/N_1N_2N_3H) \sum_R \sum_t \sum_{\kappa \text{ in } \{\kappa\}} \sum_{\lambda \text{ in } \{\lambda\}} \times \exp\{2\pi i(\lambda-\kappa)(\mathbf{t}+\tau_R)\} \times \chi_j^{\{K\}}\chi_l^{\{K\}}\chi_i^{*f.g.}(R)\delta_{R\kappa,\kappa}\delta_{R\lambda,\lambda}. \quad (17)$$

This can be contracted as described in a preceding paragraph, with the result that

$$a_i^{f.g.} = (1/k) \sum_{K \text{ in } \{K\}} \chi_j^{*\{K\}}\chi_l^{\{K\}}\chi_i^{f.g.}(K). \quad (18)$$

This is as far as the analysis for combinations and differences can be taken in general form. We can, however, proceed to one further conclusion of outstanding practical significance and this will be set forth in the following paragraph.

Most of the vectors κ will not be contained in elements of symmetry. Accordingly, the sets $\{\kappa\}$ of which they are members will contain H vectors each and will be associated with the trivial subgroup, $\{K\} = C_1$. For such an H-dimensional irreducible representation we see that

$$a_i^{f.g.} = \chi_i^{f.g.}(E). \quad (19)$$

That is, the direct product of an H-dimensional irreducible representation of the space group with itself will contain all factor group and thus all activity representations of the space group. This means physically that *any combination or difference involving two states which satisfy Eq. (14) and are associated with this kind of Hidimensional irreducible representation of the space group will not be forbidden, by symmetry, to appear in either spectrum or for any orientation of the crystal.*

In addition to these H-dimensional irreducible representations of the finite space group there are the others, whose sets of vectors $\{\kappa\}$ contain fewer than H members, for which the selection rules are stricter. For a large crystal, however, these other kinds of irreducible representations will constitute an asymptotically vanishing fraction of the total number; combinations and differences associated with them will probably be masked by the overwhelmingly greater number of the kind described above. Accordingly, the remaining irreducible representations of the finite space group can, at

least until experience proves the contrary, be neglected. If, for example, we consider a crystal which has $N_1=N_2=N_3=N$, the number of H-dimensional representations of the kind we have considered will grow with large N as N^3. At the opposite extreme, the number of factor group representations will remain constant. Intermediate between these, the other kinds of irreducible representations will grow in numbers as N and N^2. The numbers of normal coordinates associated with each of these several types of irreducible representations will grow at corresponding rates.

Of particular interest are composite transitions involving a "molecular" frequency and a lower-lying lattice mode, for these will determine band envelopes and background. Our rules predict that active fundamentals will be accompanied by combinations between lattice modes and motions from the same frequency distribution branch as the fundamental. Moreover, at about the frequency of an inactive fundamental which belongs to a non-activity factor group representation, there may appear combinations of lattice modes with modes from the same frequency distribution branch as the inactive fundamental. This gives rise to apparent violations of the factor group selection rules. We ascribe to this effect the Raman spectrum[11] of NaCl and the infra-red spectrum of diamond,[12] neither of which may contain fundamentals.

While the space group selection rules developed in this section permit composite transitions corresponding to all pairs, etc., of branches of the frequency distribution, there is, of course, no indication of the relative intensities to be expected. This latter kind of information must be obtained from a treatment requiring a detailed knowledge of the interactions. In the absence of such knowledge, we propose that the factor group selection rules, which are stricter, be used as a guide in identifying the more prominent composite transitions. That is, if a transition involving two factor group modes is forbidden, we shall assume that any transitions arising from the corresponding pair of frequency distribution branches will be less prominent than otherwise.

Those composite transitions which correspond to difference bands will be sensitive to temperature, because the population of the lower state will depend on a Boltzmann factor. This temperature sensitivity offers a means of identifying the contribution of difference bands to the spectrum.

CONCLUSIONS

The methods outlined here are adequate to give an account of the fundamentals observed in the spectra of crystals. It has been shown that the analyses according to the different kinds of symmetry groups which may be used lead to concordant results. However, it seems to us that quantitative elucidation of the breadth and fine structure of spectral lines, which involves a consideration of composite transitions, is likely to come about only by application of a stochastic method. Born and Bradburn[13] were able roughly to reproduce the fine structure of Rasetti's Raman photograph for NaCl by using Kellerman's calculated frequency distribution and adjusting a number of constants. It remains to be seen if the process can be reversed and information about the frequency distribution be obtained from the observed fine structure.

[11] E. Fermi and F. Rasetti, Zeits. f. Physik **71**, 689 (1931).
[12] G. B. B. M. Sutherland and H. A. Willis, Trans. Faraday Soc. **41**, 289 (1945).
[13] M. Born and M. Bradburn, Nature **156**, 567 (1945).

Determination of the Density of UF_6 from the Sinking Temperatures of Glass Floats

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By observing the temperatures at which glass bodies were just equal in density to the liquid, the density of liquid UF_6 was measured along the saturation curve from the triple point (64.052°C) to 162.59°C. The density of the liquid at the triple point was found to be 3.630 g cm^{-3}. Results of an earlier investigation are also reported. They confirm the later data, and lead to a value of 4.87 g cm^{-3} for the density of the solid at 62.5°C.

THE data presented in this paper were obtained during 1942 and 1943 in two separate investigations in the Low Temperature Laboratory of the National Bureau of Standards. The two investigations have been described in reports A-456 and A-1591 to the OSRD.

EXPERIMENTAL

Two different experimental methods were employed. In the first and less accurate investigation, the UF_6 was contained in a straight vertical tube in which the length of the column of liquid could be observed as a function of temperature. The material in the tube could also be frozen, and thus the relative densities near the triple point were obtained. The second and more accurate investigation dealt only with the liquid. In this investigation the liquid UF_6 was contained in a larger vertical glass tube which also contained six glass bodies (bobbins); see Fig. 1. The figure shows this tube connected to the supply cylinder ready for transfer of UF_6 into or out of it.

Measurements employing the second method were made after disconnecting the bobbin tube (Fig. 1) just beyond the first valve and placing it in a stirred liquid bath whose temperature could be accurately adjusted and controlled. This bath was contained in an unsilvered Dewar flask. Its temperature was determined with a platinum resistance thermometer whose coil was shielded from light by aluminum foil wrapped around the glass thermometer case. By slowly raising the temperature and thus gradually reducing the density of the UF_6, the lowest bobbin was made to sink. Then the temperature was gradually lowered until the bobbin rose again. This cycle was repeated several times; then the temperature was raised until measurements could be made on the bobbin just above, and so on until all the bobbins had been measured. The bobbins were cut from glasses furnished us by the Glass Section of this Bureau, and were in the form of cylinders (length: 13 mm, diameter: 9.5 mm). One glass was specially prepared for us by J. C. Young and R. L. Brownell. Densities of the bobbins, as determined by the Density Section of this Bureau, are given in Table I. This table also contains cubical expansion coefficients furnished us by the Glass Section. Bobbin densities were measured before the bobbins were used and were remeasured between runs 1 and 2. The largest discrepancy in the two sets of measurements was only 1 part in 2900.

The bobbin tube was rather heavy, as the vapor pressure of the material at the highest temperature reached was estimated to be almost 13 atm. At the top the tube joined to a small U-tube containing KF as a getter, which in turn was attached through a copper-to-glass seal to a Teflon-packed brass valve with a stainless steel needle. This assembly was pressure-tested to 25 atmos. (abs.) at 190°C and as an additional precaution a $\frac{3}{4}$-inch glass plate was placed in front of the apparatus during measurements. The KF getter was activated by heating in vacuum at 300°C, and the supply cylinder was purged of all material volatile at dry ice temperature. Then connections were made as in Fig. 1 and sufficient liquid distilled into the tube to float all the bobbins with the lowest 3 or 4 cm above the bottom of the tube. The U-tube at T jacketed the transfer line. By drawing bath liquid through it occasionally the line was kept above the temperature at which UF_6 solidifies (64.052°C).

The apparatus used in the first investigation also employed a stirred bath contained in an unsilvered Dewar flask, but the bath occupied only the lower half of the flask. The air in the upper half could be warmed by a separate heater. Then when the UF_6 was to be frozen, the air space was kept slightly above the triple point and the water bath from 5 to 10 degrees below the triple point. The sample tube had an inside diameter of approximately 3 mm and a length of 123 mm. The material, when liquid, occupied about 80 mm of the tube. It was frozen by lowering it slowly from the hot air space into the cooler water bath. Successful freezing, without the trapping of gas bubbles in the solid, took from 4 to 5 hours. Measurements of the expansivity of the liquid were made in this apparatus

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TABLE I. Densities and cubical expansion coefficients (β) of the glass bobbins.

Bobbin No.	Density at 23°C g cm^{-3}	β deg.$^{-1}$
6	3.608	27×10^{-6}
5	3.582	32
4	3.459	28
3	3.325	29
2	3.192	27
1	2.932	29

with the sample tube entirely submerged in the water bath. The length occupied by liquid was determined with a traveling microscope, by measuring the position of the meniscus relative to a fiducial scratch on the sample tube.

RESULTS

The density values obtained with the apparatus employing glass bobbins are given in Table II. The observed densities are those of the bobbins as given in Table I but corrected for thermal expansion from the temperature of calibration (23°C) to the temperatures of the various observations. Effect of pressure on the density of the bobbins was negligible, a reasonable value of the compressibility of glass (25×10^{-7} (kg cm^{-2})$^{-1}$) indicating an increase of only 3 parts in 100,000 at the highest pressure encountered. Each temperature of sinking is the lowest of several values obtained while slowly and steadily raising the temperatures of the bath, and conversely for each temperature of rising. There was no overlapping of sinking temperatures with rising temperatures. In run 1, bobbins 5 and 6 became wedged in the bottom of the sample tube and so could not be measured. Bobbin 1 was not measured because the pressure would have been too high for the sample tube. Hence after run 1 the material was removed, the tube broken and the bobbins quickly washed to prevent etching. The second run was then made using the same bobbins in a new tube (13 mm i.d., 20 mm o.d.). The densities obtained in the second run were consistently lower than those obtained in the first run by a little less than 1 per mille. There is no obvious explanation for the difference. If it is associated with the purity of the material, the first run is probably better, as the exhaustion of decomposition products from the supply cylinder prior to the second filling may not have been complete. However, because the second run covered the entire range and the first did not, the second run was used exclusively in deriving the equation representing the density.

The equation

$$\rho=3.630-5.805\times10^{-3}(t-t_f)-1.36\times10^{-5}(t-t_f)^2$$

with $t_f=64.052$°C, represents the density of saturated liquid UF_6 within the experimental error over the range covered by the measurements. The value of t_f, the triple point temperature, was taken from the work of Brickwedde, Hoge, and Scott.[1] Deviations from this equation are given in the last column of the table. At temperatures above the range of the data the equation gives densities that are too high. Considering all the likely sources of error, it seems reasonable to expect densities calculated from the equation to be correct within 3 per mille. About a third of this uncertainty may be attributed to the measurements and the rest to possible impurity of the material. The amount of impurity is difficult to estimate. The method of handling the material was similar to that used in reference 1 where the freezing-point curve indicated 2×10^{-4} as the mole fraction of impurity. The starting material in the present work was contained in a metal cylinder rather than in glass as in the other experiment, and the distilled liquid was distinctly orange-yellow although not opaque. This would indicate the presence of some molecular complexes of the form $(KF)_x(HF)_y(UF_6)_z$. A more serious possible impurity is SiF_4, which might be expected to have a partial molal volume considerably different from that of UF_6. The 2 per mille allowance, however, would cover an impurity 10 times as large as that observed in reference 1, even with a 2 to 1 ratio of partial molal volumes.

Data obtained on liquid UF_6 in the first and less accurate investigation are given in Table III. This investigation gave values of V/V_f, the ratio of the volume V at any temperature to the volume V_f of the liquid at the triple point. These data were corrected for the change in the mass of vapor above the liquid, but not for thermal expansion of the glass tube. The latter correction would have affected the observed densities by only 1 part in 3000 in the worst case, which is much less than the experimental errors. Since $V/V_f=\rho_f/\rho$ we may take the value of ρ_f (liquid) from the equation above (3.630 g cm^{-3}) and obtain densities corresponding to the data in Table III. We may also

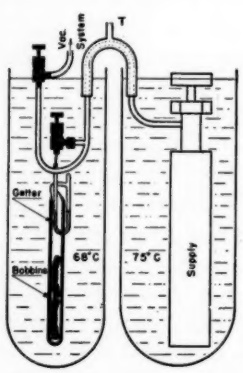

FIG. 1. Apparatus for transferring UF_6 into the experimental tube containing the bobbins. The tube was placed in a stirred liquid bath for the measurements.

[1] Ferdinand G. Brickwedde, Harold J. Hoge, and Russell B. Scott, "The low temperature heat capacities, enthalpies, and entropies of UF_4 and UF_6," J. Chem. Phys. 16, 429–36 (1948).

TABLE II. Densities of saturated liquid UF_6.*

Bobbin No.	Sinks °C	Rises °C	Av. °C	Obs. Density g cm^{-3}	Obs.-Calc. Density g cm^{-3}
			Run 1		
4	93.01	92.99	93.00	3.452	0.001
3	112.96	112.93	112.94	3.316	.002
2	131.48	131.44	131.46	3.183	.006
			Run 2		
6	68.69	68.63	68.66	3.604	.001
5	72.93	72.89	72.91	3.576	−.002
4	92.66	92.63	92.65	3.452	−.001
3	112.68	112.66	112.67	3.316	.000
2	131.17	131.07	131.12	3.183	.004
1	162.67	162.50	162.59	2.920	−.006

* Temperatures are those at which densities of UF_6 and glass bobbins became equal. Observed densities are those of the glass bobbins corrected for thermal expansion to the appropriate temperature. Calculated densities are from the equation.

calculate densities from the equation alone. "Observed" and calculated results obtained in this way (Table III, columns 3 and 4) necessarily agree at $t=t_f$, but the fact that the agreement is good throughout the range of the earlier measurements helps to corroborate both sets of data. Table III contains one value of V/V_f for the solid, at 62.5°C, which is 1.6° below the triple point. This is the most reliable of the values obtained by the process of slow freezing. Using the subsequently found value of ρ_f (liquid) the density of the solid at 62.5°C is found to be 4.87 g cm^{-3}. This value is probably correct within 5 per mille.

DISCUSSION

The density of liquid UF_6 had been measured previously by Homer F. Priest (OSRD Report A-139). His value of 3.667 g cm^{-3} at 65.1°C is higher than the value of 3.624 computed from our equation but the difference is less than his estimated error of ±0.05 g cm^{-3}. Ruff and Heinzelmann[2] found the density of solid UF_6 at 20.7°C to be 4.68, by a method involving displacement of CS_2.

The use of glass bobbins to determine density

[2] Otto Ruff and Alfred Heinzelmann, "On UF_6," Zeits. f. anorg. allgem. Chemie **72**, 63–84 (1911).

TABLE III. Values of V/V_f obtained for saturated liquid UF_6 in the first investigation.*

t °C	V/V_f	Obs. Density g cm^{-3}	Obs.-Calc. Density g cm^{-3}
		Liquid, Run A	
62.45	0.997	3.641	0.002
71.31	1.013	3.583	−0.004
73.64	1.017	3.569	−0.004
73.64	1.017	3.569	−0.004
75.98	1.022	3.552	−0.007
83.00	1.034	3.511	−0.004
85.34	1.038	3.497	−0.003
90.03	1.048	3.464	−0.006
92.38	1.053	3.447	−0.008
		Liquid, Run B	
62.45	0.997	3.641	0.002
64.03	1.000	3.630	0.000
64.97	1.001	3.626	0.001
73.64	1.016	3.573	0.000
83.00	1.033	3.514	−0.001
92.38	1.051	3.454	−0.001
		Solid	
62.5	0.745	4.87	

* Observed densities are obtained from V/V_f by using ρ_f(liquid) =3.630 from the results of the second investigation. Calculated densities are from the equation.

was particularly convenient in the present experiments because the density of the liquid permitted solid bobbins to be used. With liquids of lower density the bobbins would have to be hollow. If calibrated glass bobbins were to become readily available the method might find much wider application than has been the case up to now.

In connection with the slow freezing of the material it was found that the lower end of the sample tube could be cooled nearly 7° below the triple point before freezing started. It was also found possible to keep the entire tube 1.6° below the triple point for periods of several hours without freezing of the liquid. We had been cautioned to expect abnormal breakage in glass tubes inside which UF_6 was permitted to solidify. In the second investigation solidification was not permitted. In the first, we were relieved to find that the sample could be taken from room temperature to the triple point in the space of a few minutes without breaking the tube. This was true whether the sample was frozen slowly as described earlier or rapidly by lowering into water at room temperature.

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The Quantum Mechanics of Chemical Kinetics of Homogeneous Gas Phase Reactions*

I. General Considerations

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From the zeroth order Born-Oppenheimer approximation to the wave functions of a molecular system and the first order time-dependent perturbation theory of quantum mechanics it has been possible to deduce: (1) the adiabatic hypothesis; (2) the dependence of the rate of homogeneous gas phase chemical reactions upon the composition of reaction mixtures; (3) the condition for zero net rate of reaction, which corresponds precisely to the statistical mechanical condition for equilibrium; (4) the dependence of the chemical reaction rate upon the temperature.

Heuristic considerations transcribe the quantum mechanical result into terms of the *collision theory* and the *activated complex theory* of chemical reactions.

I. INTRODUCTION

IN any chemical reaction, one recognizes that changes may occur via a number of simultaneous and/or competing chemical and physical reactions. To make a calculation of the rate of a chemical reaction one requires, as pointed out by Wigner,[1] three somewhat different kinds of information. First, one needs to know what is the interaction between the various reactant molecules and the products formed from this interaction. Second, a knowledge is required of the rate of formation of these products from a single group of reactant molecules, this single group participating directly in a single elementary transformation, *viz.*

$$aA+bB+cC+\cdots\rightarrow pP+qQ+rR+\cdots,$$

where A, B, C, $\cdots$ represent reactant species (not necessarily the initial reactants, however), P, Q, R, $\cdots$ represent product species (possibly intermediates insofar as the over-all chemical change is concerned), and a, b, c, $\cdots$, p, q, r, $\cdots$, are integers satisfying the stoichiometry of the transformation. Third, there is required a knowledge of the interplay of the various elementary processes to give the over-all chemical reaction rate and final products.

The present paper is concerned essentially with getting information of the second kind, above.

While the quantum mechanics has been applied previously to problems of chemical kinetics,[2] certain results which have been obtained from the present study do not appear to have been obtained previously. From rather general quantum mechanical considerations of the sort used here, it is possible to deduce: (1) the adiabatic hypothesis;[3] (2) the dependence of the chemical rate upon the composition of the reacting mixture; (3) the condition for zero net rate of reaction, which corresponds precisely to the statistical mechanical condition for chemical equilibrium; (4) the dependence of the chemical reaction rate upon the temperature. The relation between the quantum mechanical results and the *collision theory* and the *activated complex theory* of chemical reaction rates is also discussed.

The two assumptions which are used in this paper are: (1) the Born-Oppenheimer[4] approximation to the wave functions of a molecular system; (2) the first order time-dependent perturbation theory of the quantum mechanics.[5] The results obtained here are, therefore, approximate. However, extension to include higher order terms of the approximation may be carried out, formally at least.

In a subsequent paper it is planned to apply the present formulation to calculate the absolute rate of a simple displacement reaction between a diatomic molecule and an atom.

II. PRELIMINARIES

Consider a system of nuclei and electrons which exist in a stationary state with respect to the energy. Schrödinger's equation for the system may be written (in atomic units):

$$[\mathbf{H}(x,\xi(\partial/\partial x))+\mathbf{T}(\partial/\partial\xi)]\Psi(x,\xi)=E\Psi(x,\xi), \quad (1)$$

where x refers to electron coordinates, ξ refers to

* This paper represents one of the results of the research program on chemical kinetics being carried out at Hydrocarbon Research, Inc.

[1] E. Wigner, Trans. Faraday Soc. **34**, 29 (1938).

[2] See for example, S. Roginsky and L. Rosenkewitsch, Zeits. f. Physik. Chemie **B10**, 47 (1930), **B15**, 103 (1931); M. Born and J. Franck, Nachr. Götting. Ges. **77** (1930); M. Born and V. Weisskopf, Zeits. f. Physik. Chemie **B12**, 206 (1931). These papers are perhaps most closely related to the treatment employed here. There is, of course, a tremendous literature on the subject, which cannot be given here. See, however, R. Oppenheimer, Phys. Rev. **31**, 66 (1928); **31**, 349 (1928); also H. Hellmann, *Quantenchemie* (Edwards Bros., Ann Arbor, Michigan, 1944), pp. 320–328.

[3] F. London, "Probleme der modernen Physik (Sommerfeld Festschift)" (1928), p. 104; Zeits. f. Electrochemie **35**, 552 (1929). See, in particular, H. Pelzer and E. Wigner, Zeits. f. Physik. Chemie **B15**, 445 (1932).

[4] M. Born and R. Oppenheimer, Ann. d. Physik **84**, 457 (1927).

[5] See, for example, P. A. M. Dirac, *The Principles of Quantum Mechanics* (Oxford University Press, London, 1947), 3rd edition, pp. 172–181.

nuclear coordinates,

$$\mathbf{H}(x, \xi, \partial/\partial x) = -\tfrac{1}{2} \sum_i (\partial^2/\partial x_i^2) + U(x, \xi),$$

$$\mathbf{T}(\partial/\partial \xi) = -\tfrac{1}{2} \sum_j (1/M_j)(\partial^2/\partial \xi_j^2),$$

$U(x, \xi)$ is the potential energy of the system.

Born and Oppenheimer[6] have shown that a good zeroth approximation to the solution of Eq. (1) may be taken as

$$\Psi_{ij}(x, \xi) = \mathrm{X}_i(x, \xi)\psi_{ij}(\xi), \tag{2}$$

where

$$\mathbf{H}(x, \xi(\partial/\partial x))\mathrm{X}_i(x, \xi) = \mathcal{U}_i(\xi)\mathrm{X}_i(x, \xi), \tag{3}$$

and

$$[\mathbf{T}(\partial/\partial \xi) + \mathcal{U}_i(\xi)]\psi_{ij}(\xi) = E_{ij}\psi_{ij}(\xi). \tag{4}$$

This approximation consists of first determining the electronic energy, $\mathcal{U}_i(\xi)$, and the electronic wave function, $\mathrm{X}_i(x, \xi)$, for various values of the (fixed) nuclear coordinates and then using this electronic energy as a potential energy function in describing the motion of the nuclei. This approximation, therefore, tacitly assumes negligible interaction between electronic and nuclear motion.

Now, from chemical evidence for the existence of distinct chemical species, it may be surmised that $\mathcal{U}_i(\xi)$ has various minima for certain values of the nuclear coordinates. This, indeed, was shown by Born and Oppenheimer to be a necessary condition for their approximation to be valid. Accordingly, the functions $\psi_{ij}(\xi)$ are to be determined in the vicinity of a particular energy minimum.

Let α denote a particular set of nuclear coordinates at which $\mathcal{U}_i(\alpha)$ is a minimum. Then by solving Eq. (4) approximately, one obtains approximate wave functions,

$$\Psi_{ij}^{(\alpha)}(x, \xi) = \mathrm{X}_i(x, \xi)\psi_{ij}^{(\alpha)}(\xi), \tag{5}$$

where the superscript denotes approximations valid in the region (α). Note that $\mathrm{X}_i(x, \xi)$ is independent of approximations that are used in determining $\psi_{ij}^{(\alpha)}(\xi)$. For a different configuration of nuclear coordinates β, one may obtain, analogously,

$$\Psi_{ij}^{(\beta)}(x, \xi) = \mathrm{X}_i(x, \xi)\psi_{ij}^{(\beta)}(\xi). \tag{6}$$

[6] M. Born and R. Oppenheimer, Ann. d. Physik **84**, 457 (1927). See also H. Hellman, *Quantenchemie* (Edwards Bros., Ann Arbor, Michigan, 1944), pp. 289–90; H. Eyring, J. Walter, and G. E. Kimball, *Quantum Chemistry* (John Wiley and Sons, Inc., New York, 1944), pp. 190–192. Note that the electronic wave functions used here differ somewhat from those used by Born and Oppenheimer. It is readily verified that the present choice corresponds to a regrouping of certain terms of the series obtained by Born and Oppenheimer, who evaluate the electronic wave function for any nuclear configuration in terms of those corresponding to an equilibrium configuration of the nuclei.

The following orthogonality conditions hold[7] (assuming normalized functions):

$$\begin{cases} \int dx \mathrm{X}_i^*(x, \xi)\mathrm{X}_j(x, \xi) = \delta_{ij}, \\ \int d\xi \psi_{ij}^{(\alpha)*}(\xi)\psi_{ik}^{(\alpha)}(\xi) = \delta_{jk}, \\ \int d\xi \psi_{ij}^{(\beta)*}(\xi)\psi_{ik}^{(\beta)}(\xi) = \delta_{jk}, \\ \int d\xi \psi_{ij}^{(\alpha)*}(\xi)\psi_{ik}^{(\beta)}(\xi) \neq \delta_{jk}. \end{cases} \tag{7}$$

When it is known that the system of nuclei and electrons are capable of forming *simultaneously* more than a single stable molecular species, a further approximation may be made by neglecting certain terms of $\mathcal{U}_i(\xi)$ that appear in Eq. (4). This, generally, will amount to an asymptotic approximation in which certain groups of nuclei are regarded as greatly removed from other groups. One may then obtain wave functions of the form

$$\Psi_{ijk}^{(\alpha)} = \mathrm{X}_i(x, \xi, \zeta)\psi_{ij}^{(\alpha)}(\xi)\varphi_{ik}^{(\alpha)}(\zeta), \tag{8}$$

where ξ and ζ denote sets of nuclear coordinates that are in remotely separated regions of space.

It can be seen that these (nuclear) wave functions are simply products of the wave functions of the various molecular species which are involved. This approximation is valid for negligible interaction among the various molecular species.

If another arrangement of the nuclei gives, again simultaneously, more than a single stable molecular species, one may obtain

$$\Psi_{lmn}^{(\beta)} = \mathrm{X}_l(x, \rho, \eta)\psi_{lm}^{(\beta)}(\rho)\varphi_{ln}^{(\beta)}(\eta), \tag{9}$$

where ρ and η denote (different) sets of nuclear coordinates that are in remotely separated regions of space, and the electronic wave function $\mathrm{X}_l(x, \rho, \eta)$ is the same as $\mathrm{X}_l(x, \xi, \zeta)$, both being solutions of Eq. (3), with merely a change of variables required to obtain one from the other.

Now, it is convenient to regard the wave functions of Eqs. (5) to (9) as arising from a set of modified Schrödinger's equations related to Eqs. (3) and (4).

In arriving at Eq. (5) as an approximation to the correct wave function, it has been tacitly assumed that the nuclear wave functions satisfy the equation

$$[\mathbf{T}(\partial/\partial \xi) + \mathcal{U}_i^{(\alpha)}(\xi)]\psi_{ij}^{(\alpha)}(\xi) = E_{ij}^{(\alpha)}\psi_{ij}^{(\alpha)}(\xi), \tag{10}$$

[7] The relations in Eq. (7) are purely formal and do not take into account the continuous spectrum of eigenvalues; in the latter case one introduces Dirac δ-functions to supplement the Kronecker deltas. This change is implied in Eq. (7).

where the superscript denotes, as above, that $\mathcal{V}_i(\xi)$ has a minimum for the nuclear configuration α. $\mathcal{V}_i^{(\alpha)}(\xi)$ may itself be regarded as the characteristic value of the equation

$$\mathbf{H}^{(\alpha)}\left(x, \xi, \frac{\partial}{\partial x}\right)\mathrm{X}_i(x, \xi) = \mathcal{V}_i^{(\alpha)}\mathrm{X}_i(x, \xi), \quad (11)$$

thus preserving a formal relation to the electronic wave equation (3). Here

$$\mathbf{H}^{(\alpha)}\left(x, \xi, \frac{\partial}{\partial x}\right) = -\tfrac{1}{2}\sum_i \frac{\partial^2}{\partial x_i^2} + U^{(\alpha)}(x, \xi), \quad (12)$$

where now the potential energy is defined so as to satisfy Eq. (11), *viz.*

$$U^{(\alpha)}(x, \xi) = \mathcal{V}_j^{(\alpha)}(\xi) + \frac{1}{2\mathrm{X}_j(x, \xi)}\sum_i \frac{\partial^2 \mathrm{X}_j(x, \xi)}{\partial x_i^2}. \quad (13)$$

Thus, when wave functions of the sort indicated in Eqs. (5)–(9) are employed, one may regard them as solutions of the many-body problem indicated in Eq. (1) with, however, the potential energy function replaced by Eq. (13).

III. DESCRIPTION OF THE REACTING SYSTEM

The following model of a reacting system will be adopted. Prior to some instant of time, which may be taken as zero with no loss of generality, the reacting molecular species will be assumed to be described by a wave function of the sort given in Eq. (8). For simplicity, no initial interaction between the molecules will be assumed, thus permitting a plane wave to be associated with the center of mass of each molecule (in the absence of any external fields). At zero time these molecules are assumed to enter a definite region of space and interact. This is equivalent to saying, for the initial instant of time, that the reacting molecules are definitely to be found in a definite region of space having the volume V. Thus the plane wave associated with each molecule is to be normalized to this volume. Hence, with the plane wave portion of the wave function displayed explicitly, the reacting system of s molecules is described initially by

$$\Psi_{ij}^{(\alpha)} = \frac{\mathrm{X}_i(x, \xi)\varphi_{ij}^{(\alpha)}(\xi)}{V^{s/2}}\prod_{k=1}^{s}\exp[(i/\hbar)\mathbf{P}_k\cdot\mathbf{r}_k], \quad (14)$$

where $\varphi_{ij}^{(\alpha)}(\xi)$ is a product wave function composed of s factors, each of which represents a wave function describing the internal nuclear motion of the individual molecular species. $\mathbf{P}_k$ and $\mathbf{r}_k$ are the linear momentum and position vectors associated with the center of mass of the kth molecule.

Considerations of a similar sort may be applied to the wave function for the products formed from the interaction. One obtains for the product system of r molecules, the final wave function,

$$\Psi_{mn}^{(\beta)} = \frac{\mathrm{X}_m(x, \xi)\varphi_{mn}^{(\beta)}(\xi)}{V^{r/2}}\prod_{l=1}^{r}\exp[(i/\hbar)\mathbf{P}_l\cdot\mathbf{r}_l]. \quad (15)$$

IV. TRANSITION PROBABILITY THEORY

The probability that a system in the configuration α will interact and undergo transitions to a configuration β may be determined using the time-dependent perturbation theory of Dirac.[5] For the present purposes, however, it is necessary to make some slight modifications of the theory.

If the interaction between the molecules of the reacting system is represented by the perturbation potential $\mathcal{H}_f'(x, \xi)$, then the probability of a transition occurring may be shown to be[8] (to a first order of approximation)

$$P(\alpha, \beta) = 2\left|\int dx d\xi \Psi_{ij}^{(\beta)*}\mathcal{H}_f'\Psi_{mn}^{(\alpha)}\right|^2 \times\left[\frac{1-\cos\{(E_\beta - E_\alpha)t/\hbar\}}{(E_\beta - E_\alpha)^2}\right]. \quad (16)$$

The integrations are to be carried out over all electronic and nuclear coordinates. E_β and E_α denote the (total) final and initial energies, respectively.

A. The Adiabatic Hypothesis

Consider the perturbation potential $\mathcal{H}_f'(x, \xi)$. Since, as indicated earlier, the choice of wave functions of the sort given in Eq. (14) implies a neglect of certain of the interactions of Eq. (3), the perturbation is simply the neglected interactions and may be taken as

$$\mathcal{H}_f'(x, \xi) = U(x, \xi) - U^{(\alpha)}(x, \xi). \quad (17)$$

To evaluate the integral in Eq. (16), it is convenient to consider first the integration over the electronic coordinates. From the previous results one obtains

$$\int dx \mathrm{X}_m^*[U(x, \xi) - U^{(\alpha)}(x, \xi)]\mathrm{X}_i(x, \xi) = [\mathcal{V}_i(\xi) - \mathcal{V}_i^{(\alpha)}(\xi)]\delta_{im}. \quad (18)$$

Thus, non-zero transition probabilities may result only if the state of the electrons remains unchanged; this is the *adiabatic hypothesis*, which it is seen follows here from the Born-Oppenheimer approximation to the total wave function for the reacting system.[9] The perturbing interaction may be regarded as depending solely upon the nuclear configuration. The perturbation consists of those terms

[8] See reference 5. Also, see the Appendix for a justification of the use of the Dirac formula in the present case.

[9] This result was very clearly demonstrated by Pelzer and Wigner,[3] who showed that the use of a wave function of the Born-Oppenheimer form leads to a time-dependent Schrödinger's equation that depends essentially upon nuclear coordinates.

which were neglected in arriving at the initial nuclear wave function (see Eqs. (4) and (10)).

B. Conservation of Energy and Momentum

The integral in Eq. (16) may be simplified by incorporating the above results. In particular, it proves convenient to introduce explicitly the centers of mass of the initial and final systems in the plane wave portion of the respective wave functions. This may be readily done, since the nuclear wave equation satisfied initially by the reactants may be separated into two equations, one involving only the coordinates of the center of mass of the entire system, the other involving *relative* nuclear coordinates. A similar statement applies to the final system of products. The plane wave portion of the wave function is simply

$$\prod_{k=1}^{s}\exp((i/\hbar)\mathbf{P}_k\cdot\mathbf{r}_k)=\left\{\prod_{k=1}^{s}\exp[(i/\hbar)\mathbf{P}_k\cdot(\mathbf{r}_k-\mathbf{r}_0)]\right\}\times\exp((i/\hbar)\mathbf{P}_\alpha\cdot\mathbf{r}_0), \quad (19)$$

where

$$\mathbf{P}_\alpha=\sum_{k=1}^{s}\mathbf{P}_k,$$

and $\mathbf{r}_0$ is the position vector of the center of mass of the system. By calling

$$\varphi_{ij}^{(\alpha)}(\xi)\prod_{k=1}^{s}\exp[(i/\hbar)\mathbf{P}_k\cdot(\mathbf{r}_k-\mathbf{r}_0)]\equiv\psi_{ij}^{(\alpha)}(\xi),$$

and similarly for the final wave function, one obtains

$$P(\alpha,\beta)=\frac{2}{V^{(r+s)}}\left|\int d\xi\psi_{mn}^{(\beta)*}[\mathcal{V}_m-\mathcal{V}_m^{(\alpha)}]\psi_{mj}^{(\alpha)}\right|^2\times\left|\int d\mathbf{r}_0\exp((i/\hbar)(\mathbf{P}_\alpha-\mathbf{P}_\beta)\cdot\mathbf{r}_0)\right|^2\times\left[\frac{1-\cos\{(E_\beta-E_\alpha)t/\hbar\}}{(E_\beta-E_\alpha)^2}\right], \quad (20)$$

where ξ denotes both relative and internal nuclear coordinates, $d\mathbf{r}_0\equiv dx_0dy_0dz_0$, where x_0, y_0, z_0 are cartesian coordinates of the center of mass.

Now

$$\int d\mathbf{r}_0\exp((i/\hbar)(\mathbf{P}_\alpha-\mathbf{P}_\beta)\cdot\mathbf{r}_0)=\int_0^{V^{1/3}}dx_0\exp((i/\hbar)\Delta P_{x_0}x_0)\times\int_0^{V^{1/3}}dy_0\exp((i/\hbar)\Delta P_{y_0}y_0)\times\int_0^{V^{1/3}}dz_0\exp((i/\hbar)\Delta P_{z_0}z_0), \quad (21)$$

where, for simplicity, a cube of side $V^{1/3}$ has been taken for the volume V, and $\mathbf{P}_\alpha-\mathbf{P}_\beta\equiv\Delta\mathbf{P}$. Carrying out the integrations and substituting in Eq. (20), one obtains

$$P(\alpha,\beta)=\frac{16\hbar^6}{V^{(r+s)}}\left|\int d\xi\psi_{mn}^{(\beta)*}[\mathcal{V}_m-\mathcal{V}_m^{(\alpha)}]\psi_{mj}^{(\alpha)}\right|^2\times\left[\frac{1-\cos(\Delta Et/\hbar)}{(\Delta E)^2}\right]\times\prod_{i=x_0,\,y_0,\,z_0}\left[\frac{1-\cos(\Delta P_iV^{1/3}/\hbar)}{(\Delta P_i)^2}\right]. \quad (22)$$

Now the last four factors are, for reasonably large volumes and time, essentially zero unless the change in energy *and* momentum is essentially zero. This is the quantum mechanical statement of *conservation of energy* and *conservation of momentum*, which might have been expected on the basis of classical considerations.

Since the final translational states have a continuous energy and momentum spectrum, it is appropriate to consider a transition from a given initial state to that range of states having their energy and momentum nearly equal to the initial energy and momentum. (All other final states have essentially zero transition probabilities.)

If the number of states having energies and momenta, as well as other quantities determining the state, in a specified range of these quantities is

$$dn=\rho_\beta(E_\beta,\mathbf{P}_\beta)dE_\beta d\mathbf{P}_\beta d\Omega_\beta, \quad (23)$$

where $d\Omega_\beta$ represents the differential of other variables upon which the number of states may depend, then the probability of a transition occurring from a given initial state to the indicated range of final states is obtained by integrating over all final states,[10]

$$\int P(\alpha,\beta)dn=\int d\Omega_\beta\int P(\alpha,\beta)\rho_\beta(E_\beta,\mathbf{P}_\beta)dE_\beta d\mathbf{P}_\beta. \quad (24)$$

Since the initial energy and momentum are regarded as fixed, it is convenient to make the change of variables,

$$\frac{dE_\beta d\mathbf{P}_\beta}{(\Delta E)^2\prod_i(\Delta P_i)^2}=\frac{tV}{\hbar^4}\frac{d(\Delta Et/\hbar)}{(\Delta Et/\hbar)^2}\prod_{i=x_0,\,y_0,\,z_0}\frac{d(\Delta P_iV^{1/3}/\hbar)}{(\Delta P_iV^{1/3}/\hbar)^2},$$

whereupon the integration of Eq. (24), after substitution of Eq. (22), is readily carried out. Four factors appear in the integral each of which is of

[10] See for example, W. Pauli, *Handbuch der Physik*, second edition, Vol. **24**, Section 1, p. 160 (1933).

the form

$$[(1-\cos x)/x^2]dx.$$

For sufficiently large time and volume, one may evaluate the remaining portion of the integrand at the origin, and extend the limits of integration from $(-\infty)$ to $(+\infty)$, with no great loss of accuracy. When the indicated operations are carried out,

$$\int P(\alpha,\beta)dn=\int d\Omega_\beta\left[\frac{16th^2\pi^4}{V^{(r+s-1)}}\rho_\beta(E_\alpha,\mathbf{P}_\alpha)\times\left|\int d\xi\psi_{mn}{}^{(\beta)*}[\mathcal{U}_m-\mathcal{U}_m{}^{(\alpha)}]\psi_{mj}{}^{(\alpha)}\right|^2\right]. \quad (25)$$

In the following section, an expression will be considered for $\rho_\beta(E_\beta,\mathbf{P}_\beta)$.

C. Density of Translational States

The number of final translational states having energies and momenta in the range of specified values of these quantities may be determined from the classical phase space occupied by the system, if the volume in which the system is contained is moderately large. For example, for r[11] molecules, $n=$ No. of translational states

$$=\frac{1}{h^{3r}}\int\cdots\int dp_1{}^\beta\cdots dp_{3r}{}^\beta dq_1{}^\beta\cdots dq_{3r}{}^\beta$$

where $p_i{}^\beta$ and $q_i{}^\beta$ are, respectively, cartesian components of momentum and position. Then the number of translational states having momenta in a specified range, but corresponding to systems that may be found anywhere in V,

$$dn=(V^r/h^{3r})dp_1{}^\beta\cdots dp_{3r}{}^\beta.$$

This result must be modified if some of the products are identical chemical species. As is known,[12] when identical particles are being considered the correct number of states is obtained from the classical phase volume by dividing by $\prod_j(\tau_j)!$, where τ_j is the number of molecules of the jth sort. Thus

$$dn=\frac{V^r}{h^{3r}\prod_j(\tau_j)!}dp_1{}^\beta\cdots dp_{3r}{}^\beta$$

with $\sum_j\tau_j=r$.

[11] The present section tacitly assumes $r\geqslant 2$. Otherwise E_β and $\mathbf{P}_\beta$ are not independent. When $r=1$ it is more convenient to integrate over a range of *initial states* in contrast to the present procedure. This can be accomplished if the number of reactant molecules $s\geqslant 2$, and the final results are unaffected. However, when both $r=s=1$ a very special case occurs, which may have to do with the peculiarities observed in homogeneous first-order *intramolecular* reactions.

[12] See for example, J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (John Wiley and Sons, Inc., New York, 1940), p. 66.

Now since the final total momentum and final energy are independent of each other and of the momentum coordinates of each molecule, a change of variables may be made so that

$$dp_1{}^\beta\cdots dp_{3r}{}^\beta=\frac{\partial(p_1{}^\beta,\cdots,p_{3r}{}^\beta)}{\partial(\mathbf{P}_\beta,E_\beta,\pi_1,\cdots,\pi_{3r-4})}d\pi_1\cdots d\pi_{3r-4}dE_\beta d\mathbf{P}_\beta,$$

where $[\partial(p_1{}^\beta,\cdots,p_{3r}{}^\beta)/\partial(\mathbf{P}_\beta,E_\beta,\pi_1,\cdots,\pi_{3r-4})]$ is the Jacobian of the transformation and π_i is a suitable function of the $p_i{}^\beta$'s. Hence

$$dn=\frac{V^r}{h^{3r}\prod_j(\tau_j)!}\times\left\{\frac{\partial(p_1{}^\beta,\cdots,p_{3r}{}^\beta)}{\partial(\mathbf{P}_\beta,E_\beta,\pi_1,\cdots,\pi_{3r-4})}d\pi_1\cdots d\pi_{3r-4}\right\}\times dE_\beta d\mathbf{P}_\beta, \quad (26)$$

which, by comparison with Eq. (23) gives $\rho_\beta(E_\beta,\mathbf{P}_\beta)d\Omega_\beta$.

Calling the quantity in braces $d\Omega_\beta$,

$$\rho_\beta(E_\beta,\mathbf{P}_\beta)=\frac{V^r}{h^{3r}}\cdot\frac{1}{\prod_j(\tau_j)!}, \quad (27)$$

and substituting in Eq. (25), one obtains

$$\int P(\alpha,\beta)dn=\frac{4t\pi^2}{h^{3r-2}V^{s-1}\prod_j(\tau_j)!}\times\int d\Omega_\beta\left|\int d\xi\psi_{mn}{}^{(\beta)*}[\mathcal{U}_m-\mathcal{U}_m{}^{(\alpha)}]\psi_{mj}{}^{(\alpha)}\right|^2. \quad (28)$$

V. THE AVERAGE RATE OF CHEMICAL TRANSITIONS

The quantity in Eq. (28) is the probability of a transition occurring from a definite initial state in the configuration α to a final range of states of the configuration β. It is important to recognize that there are, in general, a number of the latter, depending upon the possible discrete states in the energy spectrum of the final configuration. To obtain the probability of a transition occurring from molecular species in the configuration α to molecular species in the configuration β, it is necessary to sum over all final discrete states (the continuous states already having been taken into account in Eq. (28)). Finally, to obtain a result representative of experimental conditions, it is necessary to average over the initial distribution of states (both discrete and continuous). For simplicity, the initial distribution of states will be taken to be canonical (Gibbsian).[13]

[13] In what follows it is tacitly assumed that a summation over the electronic states is carried out.

Since the probability in Eq. (28) depends both upon discrete and continuous energy states, it will make for less ambiguity to express this dependence in a more explicit manner. Denoting the discrete states by a single *latin letter* and the continuous states by a single *greek letter*, Eq. (28) will be transcribed,

$$\int P(\alpha, j, \nu; \beta, k, \mu)dn = \frac{4\pi^2 t}{h^{3r-2} V^{s-1} \prod_j (\tau_j)!} \times \int d\Omega_\beta(\mu) |I(\alpha, j, \nu; \beta, k, \mu)|^2, \quad (28a)$$

where I replaces the integral in Eq. (28).

Carrying out the operations indicated above, the average probability of a chemical transition having occurred is

$$\bar{P}(\alpha, \beta) = \kappa^{(\alpha)} t Q^{(\alpha)} V^{s-1},$$

where

$$\kappa^{(\alpha)} = \frac{4\pi^2}{h^{3(r+s)-2} \prod_j (\tau_j)!} \times \sum_j{}' \exp(-E_j^{(\alpha)}/kT) \sum_k{}' \int d\Omega_\beta(\mu) \times \int dp_1{}^\alpha \cdots dp_{3s}{}^\alpha |I|^2 \exp(-E_\nu^{(\alpha)}/kT); \quad (29)$$

$$Q^{(\alpha)} = \frac{1}{h^{3s}} \sum_j \exp(-E_j^{(\alpha)}/kT) \times \int dp_1{}^\alpha \cdots dp_{3s}{}^\alpha \exp(-E_\nu^{(\alpha)}/kT), \quad (30)$$

the *partition function* of the reacting system, except for the integral over configuration space. The *average rate* of chemical transition is obtained by differentiating $\bar{P}(\alpha, \beta)$ with respect to time. Since the probability is simply proportional to time, the average rate is

$$k' = [\bar{P}(\alpha, \beta)/t]. \quad (31)$$

Specifically, Eq. (31) gives the rate of transition for a *single* reacting system to be found in the volume V.

A. Dependence of the Rate Upon The Composition of Reaction Mixtures

It is possible at this point to determine how the average rate of chemical transitions depends upon the numbers of the individual reactant species.

Equation (24) gives the probability of a single reacting system (in the volume V) making a chemical transition. The total number of transitions may be determined by multiplying this probability by the number of reactant systems in the volume V.

If there are s molecules involved in the transition, such that σ_i of the ith sort are involved and $\sum_i \sigma_i = s$, then the number of reactant systems is

$$N^{(\alpha)} = \prod_i \binom{N_i^{(\alpha)}}{\sigma_i}, \quad (32)$$

where $N_i^{(\alpha)}$ is the number of ith molecules in the volume V, and $\binom{N_i^{(\alpha)}}{\sigma_i}$ is the number of different combinations of $N_i^{(\alpha)}$ things taken σ_i at a time. Since

$$\binom{N_i^{(\alpha)}}{\sigma_i} = \frac{(N_i^{(\alpha)})!}{(N_i^{(\alpha)} - \sigma_i)!(\sigma_i)!} = \frac{N_i^{(\alpha)}(N_i^{(\alpha)} - 1) \cdots (N_i^{(\alpha)} - \sigma_i + 1)}{(\sigma_i)!},$$

it is readily seen that for $N_i^{(\alpha)}$ very large and σ_i small (as will generally be the case)

$$N^{(\alpha)} \cong \prod_i ((N_i^{(\alpha)})^{\sigma_i}/(\sigma_i)!). \quad (33)$$

The number of chemical transitions which have occurred in volume V is now given by $\bar{P}(\alpha, \beta)N^{(\alpha)}$, and the rate at which they occur is $(\bar{P}(\alpha, \beta)N^{(\alpha)}/t)$. The rate at which transitions occur *per unit volume* is then given by

$$k_f = \frac{\bar{P}(\alpha, \beta)N^{(\alpha)}}{tV} = \frac{\kappa^{(\alpha)}}{Q^{(\alpha)}} \prod \frac{1}{(\sigma_i)!} \left(\frac{N_i^{(\alpha)}}{V}\right)^{\sigma_i}, \quad (34)$$

where $\kappa^{(\alpha)}$ is defined by Eq. (29). Thus, as is known experimentally, the rate of an homogeneous chemical reaction (expressed as number of transitions per unit time and per unit volume) depends upon the *concentrations* of the reactant species.[14] It is interesting to note that this result follows directly from the *conservation of total momentum* and does not require details concerning the perturbation or the wave functions. Since total momentum is conserved only in a quantum mechanical sense, the derivation indicates that Eq. (34) will become invalid if V becomes too small.

[14] Note that this conclusion requires that the indicated matrix elements of Eq. (29) be independent of the volume. Since the perturbation vanishes asymptotically, as do the wave functions, this seems entirely reasonable. Whether or not *activities* should be used in place of concentrations is not discernable here, since the model treats the reactants as ideal gases prior to reaction.

B. Chemical Equilibrium

A necessary consequence of a proper model of chemical kinetics is that the statistical mechanical condition for chemical equilibrium be obtained when the net rate of a chemical reaction vanishes, (i.e., the difference between the forward and reverse rates) is equal to zero; in other words when[15]

$$\frac{\kappa^{(\alpha)}}{Q^{(\alpha)}}\prod_i \frac{1}{(\sigma_i)!}\left(\frac{N_i^{(\alpha)}}{V}\right)^{\sigma_i}=\frac{\kappa^{(\beta)}}{Q^{(\beta)}}\prod_j \frac{1}{(\tau_j)!}\left(\frac{N_j^{(\beta)}}{V}\right)^{\tau_j}, \quad (35)$$

where the quantities involving the β superscript are defined analogous to those involving the α superscript, and correspond to the final state or reverse reaction.

According to Eq. (29)

$$\kappa^{(\alpha)}=\frac{4\pi^2}{h^{3(r+s)-2}\prod_n(\tau_n)!}\times\sum_j{}'\exp(-E_j^{(\alpha)}/kT)\sum_k{}'\int d\Omega_\beta(\mu)\times\int dp_1{}^\alpha\cdots dp_{3s}{}^\alpha\exp(-E_\nu^{(\alpha)}/kT)\times|I(\alpha,j,\nu;\beta,k,\mu)|^2. \quad (36)$$

Correspondingly,[16]

$$\kappa^{(\beta)}=\frac{4\pi^2}{h^{3(r+s)-2}\prod_m(\sigma_m)!}\times\sum_k{}'\exp(-E_k^{(\beta)}/kT)\sum_j{}'\int d\Omega_\alpha(\nu)\times\int dp_1{}^\beta\cdots dp_{3r}{}^\beta\exp(-E_\mu^{(\beta)}/kT)\times|I(\beta,k,\mu;\alpha,j,\nu)|^2. \quad (37)$$

Now, as indicated by the primes, the summation (and integration) extends only over those values of k, μ and j, ν for which the energies and the total momenta of the initial state and final state are equal. Thus the summation extends over those values of k, μ, j, ν for which

$$\mathbf{P}_\alpha=\mathbf{P}_\beta, \quad (38)$$

and

$$E_j^{(\alpha)}+E_\nu^{(\alpha)}+E_0^{(\alpha)}=E_k^{(\beta)}+E_\mu^{(\beta)}+E_0^{(\beta)},$$

where E_0 is the zero point energy of the reactants or products, as the case may be, referred to zero energy for the completely dissociated, non-moving molecules.

Combining these results with those of Eqs. (26) and (27), one obtains[13]

$$\frac{\kappa^{(\alpha)}}{\prod_i(\sigma_i)!}\Big/\frac{\kappa^{(\beta)}}{\prod_j(\tau_j)!}=\frac{\sum_j{}'\sum_k{}'\int d\Omega_\beta(\mu)d\Omega_\alpha(\nu)dE_\nu{}^{(\alpha)}d\mathbf{P}_\alpha|I|^2\exp[-(E_j^{(\alpha)}+E_\nu^{(\alpha)})/kT]}{\sum_k{}'\sum_j{}'\int d\Omega_\alpha(\nu)d\Omega_\beta(\mu)dE_\mu{}^{(\beta)}d\mathbf{P}_\beta|I|^2\exp[-(E_k^{(\beta)}+E_\mu^{(\beta)})/kT]},$$

$$=\exp[(E_0{}^{(\alpha)}-E_0{}^{(\beta)})/kT]. \quad (39)$$

Substituting this result into Eq. (35), one obtains

$$K_e=\frac{\prod_j(N_j^{(\beta)}/V)^{\tau_j}}{\prod_i(N_i^{(\alpha)}/V)^{\sigma_i}}=\frac{Q^{(\beta)}}{Q^{(\alpha)}}\exp[(E_0{}^{(\alpha)}-E_0{}^{(\beta)})/kT]. \quad (40)$$

By including the volume factors with the Q's and recognizing that $V^sQ^{(\alpha)}=\prod_i(f_i)^{\sigma_i}$, where f_i is the partition function for a single molecule of the ith sort, and similarly for $V^rQ^{(\beta)}$, one may obtain the known[17] result for chemical equilibrium, that

$$\frac{\prod_j(N_i^{(\beta)})^{\tau_j}}{\prod_i(N_i^{(\alpha)})^{\sigma_i}}=\frac{\prod_j(f_j^{(\beta)})^{\tau_j}}{\prod_i(f_i^{(\alpha)})^{\sigma_i}}\times\exp[(E_0{}^{(\alpha)}-E_0{}^{(\beta)})/kT]. \quad (41)$$

C. Dependence of the Rate Upon the Temperature

Experimentally, one of the most important quantities affecting the rate of a chemical reaction is the temperature of the reaction mixture. It is not possible to obtain the exact dependence of the rate upon the temperature without specifying the reacting system in some detail. Nevertheless, it is possible to get a qualitative idea of what this depend-

[15] It is tacitly assumed that the products of the forward reaction are thermally equilibrated before the reverse reaction occurs.

[16] It is shown in the Appendix that the matrix elements of Eq. (37) are equal to those of Eq. (36). See Eqs. (A-9) and (A-11) of the Appendix.

[17] See for example, reference 11, p. 206.

ence is. The considerations follow the line of reasoning used by Tolman.[18]

Consider the quantity (see Eq. (34))

$$kT^2\frac{\partial \ln k_f}{\partial T}=kT^2\left[\frac{\partial \ln \kappa^{(\alpha)}}{\partial T}-\frac{\partial \ln Q^{(\alpha)}}{\partial T}\right].$$

Substituting Eq. (40), and utilizing the expression

$$kT^2\frac{\partial \ln Q^{(\alpha)}}{\partial T}=\bar{E}^{(\alpha)},$$

the average energy of the reactants, one obtains

$$kT^2\frac{\partial \ln k_f}{\partial T}=\frac{\sum_j{}'\sum_k{}'\int\cdots\int(E_j^{(\alpha)}+E_\nu^{(\alpha)})\exp[-(E_j^{(\alpha)}+E_\nu^{(\alpha)})/kT]|I|^2 d\Omega_\beta(\mu)dp_1{}^\alpha\cdots dp_{3s}{}^\alpha}{\sum_j{}'\sum_k{}'\int\cdots\int\exp[-(E_j^{(\alpha)}+E_\nu^{(\alpha)})/kT]|I|^2 d\Omega_\beta(\mu)dp_1{}^\alpha\cdots dp_{3s}{}^\alpha}-\bar{E}^{(\alpha)}. \quad (42)$$

The first quantity on the right is a sort of average energy associated with the reacting system. From Eq. (39) it is clear that if one includes the zero point energy E_0 with the partition function for the reactants (or products, as the case may be) then the first term of Eq. (42) will be the same for either the forward or reverse reaction. Hence, one may write

$$kT^2(\partial \ln k_f/\partial T)=E^\dagger-(\bar{E}^{(\alpha)}+E_0{}^{(\alpha)}), \quad (43)$$

where $E^\dagger$ is an energy term that is the same for both the forward and reverse reactions. For the reverse reaction β replaces α.

If the quantity on the right-hand side of Eq. (43) does not depend strongly upon the temperature, so that for some range of temperature

$$E^\dagger-(\bar{E}^{(\alpha)}+E_0{}^{(\alpha)})\doteq E^*+\epsilon(T),$$

where $\epsilon(T)$ is small compared to E, one obtains

$$k_f\sim A(T)\exp(-E^*/kT)\prod_i(N_i^{(\alpha)}/V)^{\sigma_i}, \quad (44)$$

analogous to the Arrhenius equation,[19] except for the dependence of A upon the temperature.

VI. HEURISTIC CONSIDERATIONS

A transcription of the quantum mechanical results into the language of the *collision theory* or the *activated complex theory* of reaction rates is highly desirable inasmuch as both of these theories have provided the subject with extremely useful models of the course of chemical reactions. A deductive transcription does not, however, seem possible. Nevertheless, with the knowledge of the form assumed by both of these theories, one can arrange the quantum mechanical expression so that a correspondence may be made with each of them.

A. The Collision Theory

While the theory developed here deals exclusively with transitions that result in chemical change, a restriction of this sort is really unnecessary. Those interactions which result simply in the change of (quantum) state of the reactants may be treated as entirely analogous to those which result in chemical change. Application of the previous treatment gives an expression for the *number of collisions per unit time per unit volume,*

$$n=(\kappa_{\text{coll.}}{}^{(\alpha)}/Q^{(\alpha)})\prod_i(1/(\sigma_i)!)(N_i{}^{(\alpha)}/V)^{\sigma_i},$$

where

$$\kappa_{\text{coll.}}{}^{(\alpha)}=\frac{4\pi^2}{h^{6s-2}\prod_i(\sigma_i)!}\sum_j{}'\sum_{j'}{}'\int\cdots$$
$$\times\int\exp[-(E_j^{(\alpha)}+E_\nu^{(\alpha)})/kT]$$
$$\times|I(\alpha,j,\nu;\alpha,j',\nu')|^2$$
$$\times d\Omega_\alpha(\nu')dp_1{}^\alpha\cdots dp_{3s}{}^\alpha. \quad (45)$$

The primes indicate that summations and integration are to be made under conditions of conservation of energy and total momentum. The perturbation energy used to evaluate $I(\alpha, j, \nu; \alpha, j', \nu')$ is the same as that used for chemical transitions, *viz.*, Eq. (17).

The expression for $\kappa_{\text{coll.}}{}^{(\alpha)}$ differs from $\kappa^{(\alpha)}$ (see Eq. (36)) in three important respects. First, the matrix elements are evaluated in terms of different sets of wave functions. Second, the density of final states is different in the two cases. Third, the integrations start from significantly different values of the initial energy for those chemical transitions which are strongly endothermic. The essential assumption of the collision theory of chemical reactions is that this last difference is the most important one in distinguishing between chemical and non-chemical transitions.

This assumption may be expressed in terms of the notation of the present paper as follows: If one

[18] R. C. Tolman, J. Am. Chem. Soc. **47**, 2652 (1925).
[19] S. Arrhenius, Zeits. f. Physik. Chemie **4**, 226 (1889).

defines the function $f(j, \nu)$ by the equation

$$\left[\frac{4\pi^2}{h^{3s-2}\prod_i(\sigma_i)!}\sum_{j'}\int d\Omega_\alpha(\nu')\times|I(\alpha, j, \nu; \alpha, j', \nu')|^2\right]f(j, \nu)$$
$$=\frac{4\pi^2}{h^{3r-2}\prod_j(\tau_j)!}\sum_{k'}\int d\Omega_\beta(\mu)\times|I(\alpha, j, \nu; \beta, k, \mu)|^2, \quad (46)$$

then the collision theory asserts that

$$f(j, \nu)\sim 1 \quad \text{for} \quad E_\nu^{(\alpha)} \gtrsim E^* \gg 0,$$
$$f(j, \nu)\sim 0 \quad \text{for} \quad E_\nu^{(\alpha)} < E^*.$$

In other words, it is assumed that the intrinsic probability of a collision which does not result in chemical reaction is the same as one which does result in chemical reaction. Substituting Eq. (46) into Eq. (36), one obtains

$$\kappa^{(\alpha)} = 1/h^{3s}\int \sum_j f(j, \nu)Z(j, \nu)\times\exp[-(E_j^{(\alpha)}+E_\nu^{(\alpha)})/kT]dp_1^\alpha\cdots dp_{3s}^\alpha,$$

where $Z(j, \nu)$ is the bracketed quantity in Eq. (46). If now $f(j, \nu)Z(j, \nu)$ depends only slightly upon the internal states of the reactants (through the quantum numbers j, ν) then it can be shown that

$$\kappa^{(\alpha)}\sim\kappa_{\text{coll.}}^{(\alpha)}\exp(-E^*/kT). \quad (47)$$

Substitution of Eq. (47) into Eq. (45), together with Eq. (34) gives

$$k_f\sim n\exp(-E^*/kT), \quad (48)$$

the essential statement of the collision theory.[20] It is seen here that this result follows only if the transition probability for non-chemical transitions assumes a very special functional form that permits the above approximations to hold exactly.

B. The Activated Complex Theory

According to Eq. (39) the quantity

$$\kappa^\dagger = \frac{\kappa^{(\alpha)}}{\prod_i(\sigma_i)!}\exp(-E_0^{(\alpha)}/kT) = \frac{\kappa^{(\beta)}}{\prod_j(\tau_j)!}\exp(-E_0^{(\beta)}/kT),$$

has a value that is the same for both the forward and reverse reactions. It is convenient, therefore, to write the expression for the rate as follows:

$$k_f = \frac{\kappa^\dagger}{Q^{(\alpha)}\exp(-E_0^{(\alpha)}/kT)}\prod_i\left(\frac{N_i^{(\alpha)}}{V}\right)^{\sigma_i},$$

where now $\kappa^\dagger$ is to be regarded as a function of both the initial and final sets of states. In a sense it is a "constant" of the chemical reaction. It may be written in the suggestive form

$$\kappa^\dagger = \frac{kT}{h}\left[\frac{4\pi^2}{h^{3(r+s-1)}\prod_{m,n}(\sigma_m)!(\tau_n)!}\cdot\frac{1}{kT}\sum_{j'}\sum_{k'}\int\cdots\int d\Omega_\beta(\mu)\times\exp[-(E_j^{(\alpha)}+E_\nu^{(\alpha)}+E_0^{(\alpha)})/kT]\times|I|^2 dp_1^\alpha\cdots dp_{3s}^\alpha\right]. \quad (49)$$

The quantity in brackets has the dimensions $(\text{cm})^{-3}$. It is very closely related to a partition function (per unit volume) insofar as it contains terms of the form $e^{-E/kT}$. However it cannot, strictly speaking, be considered as such because of the quantity $|I|^2$ which, since it is not dimensionless as would be required, cannot be regarded as merely a statistical weight factor of some sort. Nevertheless, it is apparent that the bracketed quantity will have the essential properties of a partition function as regards its dependence upon the temperature. (See Section V-C on temperature dependence.)

If we set

$$Q^{(\alpha)}\exp(-E_0^{(\alpha)}/kT) \equiv Q_0^{(\alpha)},$$

the partition function (apart from volume factors) of the reactants, referred to the origin of the energy, the following suggestive expression for the rate is obtained

$$k_f = \frac{kT}{h}\frac{Q_0^\dagger}{Q_0^{(\alpha)}}\prod\left(\frac{N_i^{(\alpha)}}{V}\right)^{\sigma_i}, \quad (50)$$

a form first obtained by Eyring.[21] $Q_0^\dagger$ is the bracketed quantity in Eq. (49) and is to be identified with Eyring's *partition function for the activated complex* (multiplied by the transmission coefficient).

Whether or not one wishes to regard $Q_0^\dagger$ as a "true" partition function is of little consequence. It appears that it would not be distinguished from one experimentally.

[20] See for example, C. N. Hinshelwood, *The Kinetics of Chemical Change* (Oxford University Press, London, 1940), p. 78.

[21] H. Eyring, J. Chem. Phys. **3**, 107 (1935). See also H. Eyring, J. Walter, and G. E. Kimball, *Quantum Chemistry* (John Wiley and Sons, Inc., New York, 1944), p. 307.

VII. REMARKS

It is to be emphasized that although the present treatment involves a system of reactants which are distributed canonically with respect to the energy, and the tacit assumption that any products which are formed become canonically distributed before subsequent chemical reactions occur, this condition is by no means essential. One advantage of the present formulation is that it indicates formally just how the distribution of initial states appears in the expression for the rate. It should be interesting to study the effect of changes in distribution upon the rate. However, it appears that specific information about the matrix elements is needed.

Another advantage of the present formulation is that the distribution of the initially formed products with respect to the final states is obtainable from the equations which have been presented. This feature appears not to be contained in either the collision or activated complex theories.

The consequence that the adiabatic hypothesis follows directly from the zeroth order approximation to the wave functions for the system poses an important question: How are non-adiabatic processes possible? Clearly, one must distinguish between two kinds of non-adiabatic processes. In the first of these there exists some range of nuclear configurations for which the electronic energy levels are degenerate, or nearly so. In this case one must employ a proper linear combination of the degenerate electronic wave functions before applying the first order theory.[22] This has been implied in the present treatment and offers no difficulty. In the second kind of non-adiabatic process one must deal with transitions between non-degenerate electronic states. The present approximation does not permit of this possibility. Clearly, these transitions become possible when first order approximations to the wave functions are introduced, and second order time-dependent perturbation theory is employed.

Inasmuch as the conclusions reached in this paper depend upon the first order perturbation theory, it should be interesting to see what modifications become necessary when higher order perturbations are incorporated into the theory.

VIII. ACKNOWLEDGMENTS

The author wishes to express his appreciation to Professor E. B. Wilson, Jr. of Harvard University, for some very helpful correspondence and discussion at the beginning of this investigation. The encouragement and helpful suggestions of Drs. M. Benedict, A. M. Peiser, and A. M. Squires are gratefully acknowledged.

[22] See, for example, H. Hellmann, *Einführing in die Quantenchemie* (Edwards Bros., Ann Arbor, Michigan, 1944), p. 323.

APPENDIX

Transition Probabilities for Non-orthogonal States

Consider Schrödinger's time dependent wave equation

$$i\hbar(\partial\Psi_m/\partial t)=\mathbf{H}\Psi_m, \tag{A-1}$$

where Ψ_m depends upon all the configurational coordinates and the time, $\mathbf{H}$ is the total Hamiltonian for the system (cf. Eq. (1)) and is independent of the time.

To determine the probability of finding the system described by a wave function corresponding to the configuration β let

$$\Psi_m=\Psi_m{}^{(\alpha)}\exp[-(i/\hbar)E_m{}^{(\alpha)}t], \quad (t<0), \tag{A-2}$$

$$\Psi_m=\Sigma_n\, a_{mn}(t)\Psi_n{}^{(\beta)}\exp[-(i/\hbar)E_n{}^{(\beta)}t], \quad (t\geq 0), \tag{A-3}$$

where

$$\Sigma_n|a_{mn}(0)|^2=1.$$

Here

$$\begin{cases}\mathbf{H}^{(\alpha)}\Psi_m{}^{(\alpha)}=E_m{}^{(\alpha)}\Psi_m{}^{(\alpha)},\\ \mathbf{H}^{(\beta)}\Psi_n{}^{(\beta)}=E_n{}^{(\beta)}\Psi_n{}^{(\beta)}.\end{cases} \tag{A-4}$$

The $\Psi^{(\alpha)}$ and $\Psi^{(\beta)}$ span the same configuration space, and are assumed to be normalized to unity.

As is usually done, the probability of finding the system described by the wave function $\Psi_n{}^{(\beta)}$ is taken to be $|a_{mn}(t)|^2$. The *transition probability* will be defined as the difference between this probability and the probability that the system was described by the same wave function originally,

$$P(\alpha,\beta)=|a_{mn}(t)|^2-|a_{mn}(0)|^2. \tag{A-5}$$

Substitution of (A-3) into (A-1), gives

$$i\hbar\,\Sigma_n\,\dot{a}_{mn}\Psi_n{}^{(\beta)}\exp[-(i/\hbar)E_n{}^{(\beta)}t]=(\mathbf{H}-\mathbf{H}^{(\beta)})\Psi_m, \tag{A-6}$$

and, since the $\Psi^{(\beta)}$ form a complete orthonormal set,

$$i\hbar\dot{a}_{mn}=\left(\int d\tau\Psi_n{}^{(\beta)*}(\mathbf{H}-\mathbf{H}^{(\beta)})\Psi_m\right)\exp[(i/\hbar)E_n{}^{(\beta)}t]. \tag{A-7}$$

Equation (A-7) may be solved by an iterative procedure. By inserting Eq. (A-2) one may obtain a first approximation to $a_{mn}(t)$. One then obtains

$$a_{mn}{}^{(1)}(t)-a_{mn}(0)=\left(\int d\tau\Psi_n{}^{(\beta)}(\mathbf{H}-\mathbf{H}^{(\beta)})\Psi_m{}^{(\alpha)}\right)\times\left[\frac{1-\exp[(i/\hbar)(E_n{}^{(\beta)}-E_m{}^{(\alpha)})t]}{E_n{}^{(\beta)}-E_m{}^{(\alpha)}}\right].$$

From this, one may obtain

$$\begin{aligned}P(\alpha,\beta)&=|a_{mn}{}^{(1)}(t)|^2-|a_{mn}(0)|^2\\&=2\left|\int d\tau\Psi_n{}^{(\beta)*}(\mathbf{H}-\mathbf{H}^{(\beta)})\Psi_m{}^{(\alpha)}\right|^2\\&\quad\times\left[\frac{1-\cos\{(E_n{}^{(\beta)}-E_m{}^{(\alpha)})/\hbar\}t}{(E_n{}^{(\beta)}-E_m{}^{(\alpha)})^2}\right]\\&\quad+2\,\Re\left\{\int d\tau\Psi_m{}^{(\alpha)*}\Psi_n{}^{(\beta)}\right\}\\&\quad\times\left\{\int d\tau\Psi_n{}^{(\beta)*}(\mathbf{H}-\mathbf{H}^{(\beta)})\Psi_m{}^{(\alpha)}\right\}\\&\quad\times\left[\frac{1-\cos\{(E_n{}^{(\beta)}-E_m{}^{(\alpha)})/\hbar\}t}{E_n{}^{(\beta)}-E_m{}^{(\alpha)}}\right]\\&\quad+2\,\Im\left\{\int d\tau\Psi_m{}^{(\alpha)*}\Psi_n{}^{(\beta)}\right\}\\&\quad\times\left\{\int d\tau\Psi_n{}^{(\beta)*}(\mathbf{H}-\mathbf{H}^{(\beta)})\Psi_m{}^{(\alpha)}\right\}\\&\quad\times\left[\frac{\sin\{(E_n{}^{(\beta)}-E_m{}^{(\alpha)})/\hbar\}t}{E_n{}^{(\beta)}-E_m{}^{(\alpha)}}\right],\end{aligned} \tag{A-8}$$

where $\Re$ and $\Im$ indicate, respectively, real and imaginary parts; also $a_{mn}(0)=\int d\tau\Psi_n{}^{(\beta)*}\Psi_m{}^{(\alpha)}$, from Eqs. (A-2) and (A-3).

When an integration over the energy $E_n{}^{(\beta)}$ is carried out ($E_m{}^{(\alpha)}$ fixed), as is usually the case, the second term of the

right side of Eq. (A-8) can be made to vanish. The last term will vanish only if the indicated matrix element is real.

Since $\mathbf{H}$, $\mathbf{H}^{(\alpha)}$, and $\mathbf{H}^{(\beta)}$ may be assumed real, $\Psi_m{}^{(\alpha)}$ and $\Psi_n{}^{(\beta)}$ as well as their complex conjugates are solutions of Eq. (A-4). For distinct energy levels these wave functions can differ from their complex conjugates only by an arbitrary phase factor, in which case the indicated matrix element is real. For degenerate levels the matrix element need not be real. However, since the set of wave functions corresponding to a degenerate level may always be arranged to consist of a linearly independent set of functions and their complex conjugates, the last term of Eq. (A-8) will vanish when summed over all degenerate states.

Hence, understanding that an integration with respect to the energy is to be carried out, as well as a summation over the degenerate states, one may take

$$P(\alpha,\beta)=2\left|\int d\tau\Psi_n{}^{(\beta)*}(\mathbf{H}-\mathbf{H}^{(\beta)})\Psi_m{}^{(\alpha)}\right|^2 \times\left[\frac{1-\cos\{(E_n{}^{(\beta)}-E_m{}^{(\alpha)})/\hbar\}t}{(E_n{}^{(\beta)}-E_m{}^{(\alpha)})^2}\right]. \quad \text{(A-9)}$$

Since

$$\int d\tau\Psi_n{}^{(\beta)*}(\mathbf{H}^{(\alpha)}-\mathbf{H}^{(\beta)})\Psi_m{}^{(\alpha)}=E_m{}^{(\alpha)}\int d\tau\Psi_n{}^{(\beta)*}\Psi_m{}^{(\alpha)} -\Sigma_k\left[\int d\tau\Psi_n{}^{(\beta)*}\mathbf{H}^{(\beta)}\Psi_k{}^{(\beta)}\right]\left[\int d\tau\Psi_k{}^{(\beta)*}\Psi_m{}^{(\alpha)}\right] =(E_m{}^{(\alpha)}-E_n{}^{(\beta)})\int d\tau\Psi_n{}^{(\beta)*}\Psi_m{}^{(\alpha)}, \quad \text{(A-10)}$$

one can obtain, with the same understanding as in Eq. (A-9),

$$P(\alpha,\beta)=2\left|\int d\tau\Psi_n{}^{(\beta)*}(\mathbf{H}-\mathbf{H}^{(\alpha)})\Psi_m{}^{(\alpha)}\right|^2 \times\left[\frac{1-\cos\{(E_n{}^{(\beta)}-E_m{}^{(\alpha)})/\hbar\}t}{(E_n{}^{(\beta)}-E_m{}^{(\alpha)})^2}\right]. \quad \text{(A-11)}$$

Thus, in spite of the fact that $(\mathbf{H}-\mathbf{H}^{(\beta)})$ and $(\mathbf{H}-\mathbf{H}^{(\alpha)})$ represent entirely different perturbation functions, the transition probabilities which involve these perturbations (e.g., the forward and reverse perturbations in a chemical transition) are essentially equal.

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The Quantum Mechanics of Chemical Kinetics of Homogeneous Gas Phase Reactions*

II. Approximations for Displacement Reaction between an Atom and a Diatomic Molecule

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The quantum mechanics of a displacement reaction: $AB+C\rightarrow A+BC$, has been considered and the results have been applied to the reaction: $H_2+Br\rightarrow H+HBr$ at 500°K. The potential energy of the reacting system is based upon the London approximation as modified by Eyring and Polanyi. The absolute rate has been found to be a sensitive function of the coulombic energy fraction; when this fraction is taken to be 30 percent, the absolute rate is in essential agreement with the observed value. This agreement can only be regarded as fortuitous, however.

Several results have been derived which are not sensitive to the fraction of coulombic energy and furnish, therefore, a more stringent test of the present formulation. It has been found that the variation of the absolute rate with temperature, as calculated at 500°K, compares favorably with the observed variation. Approximately 95 percent of the rate comes from hydrogen molecules in the first excited vibrational state. The contribution from hydrogen molecules in various rotational states is given. The distribution of the initially formed hydrogen bromide molecules has been found to be representable by a pseudo-canonical distribution function of the rotational quantum number, in which the "rotational temperature" is approximately one-half the initial temperature.

I. INTRODUCTION

A QUANTUM mechanical formulation for the rate of a chemical reaction has been presented in the first paper of this series.[1] In order to apply the results of (I) to a particular chemical reaction, one needs to know the potential energy (electronic energy) of the reacting system and the wave functions of both reactants and products. For reactions involving large numbers of molecules it is difficult to obtain accurately the potential energy and the wave functions. Even in fairly simple cases, approximations must be made to all of these quantities.

In the present paper, we consider the simple example of a *displacement reaction:* $AB+C\rightarrow A+BC$. The perturbation energy is constructed from the Eyring and Polanyi[2] modification of the potential energy of a triatomic system as given by London.[3]

* This paper represents one of the results of the research program on chemical kinetics being carried out at Hydrocarbon Research, Inc.

[1] Sidney Golden, "The quantum mechanics of chemical kinetics of homogeneous gas phase reactions, I. General considerations," J. Chem. Phys. **17**, 620 (1949). This paper will be referred to as (I).

[2] H. Eyring and M. Polanyi, Zeits. f. physik. Chemie. **B12**, 279 (1931); see also, for example, S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941), pp. 85–152.

[3] F. London, *Probleme der modernen Physik* (*Sommerfeld Festschrift*) (S. Herzel, Leipzig, 1928), p. 104; Zeits f. Elektrochemie. **35**, 552 (1929).

The admittedly crude assumption is made that the A–B and B–C potentials can be approximated by harmonic oscillator potentials, and that the A–C potential can be taken as some constant value.

The results are applied to the reaction:

$$H_2+Br\rightarrow H+HBr,$$

at 500°K. The calculated value of the absolute rate is found to be sensitive to the exact value taken for the coulombic energy fraction in the Eyring—Polanyi approximation. Hence no value is given for the rate. Instead, the dependence of the calculated rate upon the coulombic energy fraction is given graphically in Fig. 1. When this fraction is between 25–30 percent, good agreement is obtained with experiment.

Several results have been derived which are not sensitive to the choice of the coulombic energy fraction. The variation of the absolute rate with temperature, as calculated at 500°K, compares favorably with the observed variation. The contribution to the rate made by each of the discrete states of the hydrogen molecule is obtained. It is found, for example, that by far the greatest contribution to the rate comes from hydrogen molecules in the first excited vibrational state. Of perhaps greater interest is the distribution among the rotational states of hydrogen bromide molecules formed. This distribution may be represented by a Gibbsian canonical form in which, however, the "rotational temperature" is significantly different from the temperature of the reactants.

II. THE WAVE FUNCTIONS

Following the model of the reacting system discussed in (I) we assume that at the initial instant of time a diatomic molecule of mass (m_1+m_2) and an atom of mass m_3 enter a region of volume V. The momentum of the initial molecule is $\mathbf{P}_{12}$, while that of the initial atom is $\mathbf{P}_3$. Subsequent to the displacement reaction, the final molecule has mass (m_2+m_3) and momentum $\mathbf{P}_{23}$, while the atom has mass m_1 and momentum $\mathbf{P}_1$.

To the approximation that interactions between translational, rotational and vibrational motion may be neglected, and with the assumption of harmonic vibrations of the molecule, the initial wave function for the reacting system may be taken as[4]

$$\psi_i=\frac{N_n}{V}\exp\left(\frac{i}{\hbar}\mathbf{P}_{12}\cdot\mathbf{r}_{12}\right)\frac{H_n(\xi)\exp(-\xi^2/2)}{[\xi/(a_1)^{\frac{1}{2}}+\rho_1]}$$
$$\times P_K^{|M|}(\cos\theta)e^{iM\varphi}\exp\left(\frac{i}{\hbar}\mathbf{P}_3\cdot\mathbf{r}_3\right). \quad (1)$$

[4] See, for example, L. Pauling and E. B. Wilson, Jr., *Introduction to Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1935), pp. 259–271.

Here $N_nH_n(\xi)e^{-\xi^2/2}$ is a normalized hermite orthogonal function. $P_K^{|M|}(\cos\theta)e^{iM\varphi}$ is a normalized spherical harmonic, representing the rotational part of the wave function. The translational wave functions have been taken as plane waves, each normalized to the volume V;

$$N_n=[(a_1/\pi)^{\frac{1}{2}}(1/2^n n!)]^{\frac{1}{2}},$$
$$a_1=(4\pi^2\mu_1\nu_1/h);$$

$\mu_1=m_1m_2/(m_1+m_2)$, the reduced mass of the initial molecule; ν_1 is the fundamental vibration frequency of the initial molecule;

$$\mathbf{r}_{12}=(m_1/(m_1+m_2))\mathbf{r}_1+(m_2/(m_1+m_2))\mathbf{r}_2,$$

the (vector) coordinate of the center of mass of the initial molecule; $(\xi/(a_1)^{\frac{1}{2}}+\rho_1)$ is the distance between atoms of the initial molecule, where ρ_1 is the equilibrium distance between the atoms of the initial molecule; $\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3$, are the (vector) coordinates of the respective atoms; θ, φ refer to the polar and azimuthal angles in spherical polar coordinates which fix the orientation of the initial molecule in space; n, K and M are quantum numbers corresponding respectively to vibration, total angular momentum, and the component of the latter along a space fixed axis.

The volume element for this wave function is

$$d\tau_i=d\mathbf{r}_{12}d\mathbf{r}_3\left(\frac{\xi}{(a_1)^{\frac{1}{2}}}+\rho_1\right)^2 d\left(\frac{\xi}{(a_1)^{\frac{1}{2}}}\right)d(\cos\theta)d\varphi, \quad (2)$$

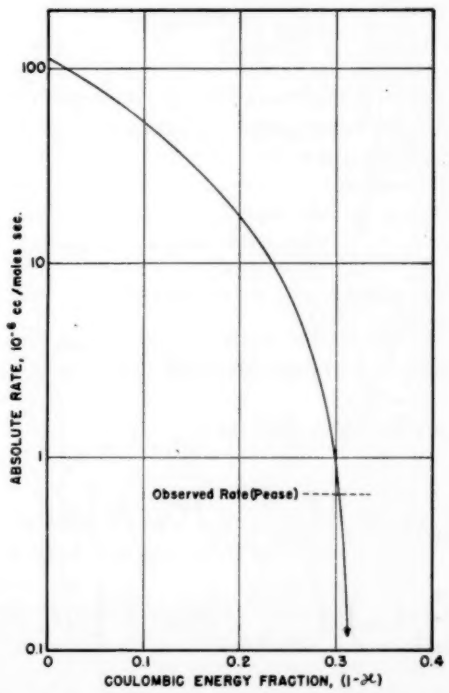

FIG. 1. Calculated variation of the absolute rate with fraction of coulombic energy.

where $d\mathbf{r}=dxdydz$ and x, y, z are the cartesian coordinates of $\mathbf{r}$. The final wave function for the reacting system may be taken as

$$\psi_f=\frac{N_m}{V}\exp\left(\frac{i}{\hbar}\mathbf{P}_{23}\cdot\mathbf{r}_{23}\right)\frac{H_m(\eta)\exp(-\eta^2/2)}{[(\eta/(a_2)^{\frac{1}{2}})+\rho_2]}$$
$$\times P_L^{|N|}(\cos\theta')e^{iN\varphi'}\exp\left(\frac{i}{\hbar}\mathbf{P}_1\cdot\mathbf{r}_1\right), \quad (3)$$

where

$$\mathbf{r}_{23}=(m_2/(m_2+m_3))\mathbf{r}_2+(m_3/(m_2+m_3))\mathbf{r}_3,$$

and other quantities are defined analogous to the previous definitions.

The volume element for this wave function is

$$d\tau_f=d\mathbf{r}_1d\mathbf{r}_{23}\left(\frac{\eta}{(a_2)^{\frac{1}{2}}}+\rho_2\right)^2d\left(\frac{\eta}{(a_2)^{\frac{1}{2}}}\right)d(\cos\theta')d\varphi'. \quad (4)$$

It is convenient to make a change of variables at this point. Noticing that

$$\mathbf{r}_1=\mathbf{r}_2+\left(\frac{\xi}{(a_1)^{\frac{1}{2}}}+\rho_1\right)\hat{\imath}(\theta,\varphi),$$

where $\hat{\imath}(\theta,\varphi)$ is a unit vector along the internuclear axis of the initial molecule, *viz.*

$$\hat{\imath}_x=\sin\theta\cos\varphi,$$
$$\hat{\imath}_y=\sin\theta\sin\varphi,$$
$$\hat{\imath}_z=\cos\theta,$$

and $\mathbf{r}_3=\mathbf{r}_2+(\eta/(a_2)^{\frac{1}{2}}+\rho_2)\hat{\jmath}(\theta',\varphi')$, where $\hat{\jmath}(\theta',\varphi')$ is a unit vector along the internuclear axis of the final molecule, *viz.*

$$\hat{\jmath}_x=\sin\theta'\cos\varphi',$$
$$\hat{\jmath}_y=\sin\theta'\sin\varphi',$$
$$\hat{\jmath}_z=\cos\theta',$$

one may show that

$$\mathbf{P}_{12}\cdot\mathbf{r}_{12}+\mathbf{P}_3\cdot\mathbf{r}_3-\mathbf{P}_1\cdot\mathbf{r}_1-\mathbf{P}_{23}\cdot\mathbf{r}_{23}$$
$$=(\mathbf{P}_{12}+\mathbf{P}_3-\mathbf{P}_1-\mathbf{P}_{23})\cdot\mathbf{r}_2$$
$$+\left(\frac{\xi}{(a_1)^{\frac{1}{2}}}+\rho_1\right)\left[\left(\frac{m_1}{m_1+m_2}\right)\mathbf{P}_{12}-\mathbf{P}_1\right]\cdot\hat{\imath}(\theta,\varphi)$$
$$+\left(\frac{\eta}{(a_2)^{\frac{1}{2}}}+\rho_2\right)\left[\left(\frac{m_3}{m_2+m_3}\right)\mathbf{P}_{23}-\mathbf{P}_3\right]\cdot\hat{\jmath}(\theta',\varphi'). \quad (5)$$

This facilitates a change to variables: $\mathbf{r}_2$, ξ, η, θ, θ', φ, φ' which gives

$$\psi_f^*\psi_i=N_nN_m\frac{H_n(\xi)\exp(-\xi^2/2)H_m(\eta)\exp(-\eta^2/2)}{\left(\frac{\xi}{(a_1)^{\frac{1}{2}}}+\rho_1\right)\left(\frac{\eta}{(a_2)^{\frac{1}{2}}}+\rho_2\right)}$$
$$\times P_K^{|M|}(\cos\theta)P_L^{|N|}(\cos\theta')\exp(iM\varphi-iN\varphi')$$
$$\times\frac{1}{V^2}\exp\frac{i}{\hbar}\left\{\Delta\mathbf{P}\cdot\mathbf{r}_2+\left(\frac{\xi}{(a_1)^{\frac{1}{2}}}+\rho_1\right)\boldsymbol{\alpha}\cdot\hat{\imath}\right.$$
$$\left.+\left(\frac{\eta}{(a_2)^{\frac{1}{2}}}+\rho_2\right)\boldsymbol{\beta}\cdot\hat{\jmath}\right\}, \quad (6)$$

where

$$\Delta\mathbf{P}=\mathbf{P}_{12}+\mathbf{P}_3-\mathbf{P}_1-\mathbf{P}_{23},$$
$$\boldsymbol{\alpha}=\left(\frac{m_1}{m_1+m_2}\right)\mathbf{P}_{12}-\mathbf{P}_1, \quad (7)$$
$$\boldsymbol{\beta}=\left(\frac{m_3}{m_2+m_3}\right)\mathbf{P}_{23}-\mathbf{P}_3.$$

In terms of the new coordinates the volume element is

$$d\tau=\left(\frac{\xi}{(a_1)^{\frac{1}{2}}}+\rho_1\right)^2\left(\frac{\eta}{(a_2)^{\frac{1}{2}}}+\rho_2\right)^2d\mathbf{r}_2d\left(\frac{\xi}{(a_1)^{\frac{1}{2}}}\right)$$
$$\times d\left(\frac{\eta}{(a_2)^{\frac{1}{2}}}\right)d(\cos\theta)d(\cos\theta')d\varphi d\varphi'. \quad (8)$$

III. THE PERTURBATION ENERGY

Although the wave functions for the reactants and the products are approximate, one can have a degree of confidence in their reliability, which is based upon their successful application in molecular spectroscopy. The perturbation, however, is an entirely different matter. Since the potential energy of an interacting system has not been subjected to direct experimental verification, there is correspondingly greater uncertainty regarding the perturbation than there is regarding the wave functions.

In order to approximate the potential energy of the reacting system, we shall employ the results of London,[3] and the particular modification of his results by Eyring and Polanyi.[2]

London's expression for the potential energy of the system ABC is given by

$$\mathcal{U}_{ABC}=Q_{AB}+Q_{BC}+Q_{AC}-(V_{AB}^2+V_{BC}^2$$
$$+V_{AC}^2-V_{AB}V_{BC}-V_{AB}V_{AC}-V_{BC}V_{AC})^{\frac{1}{2}}, \quad (9)$$

where Q and V represent the coulombic and exchange energies, respectively, of the various pairs of atoms.

The modification of Eyring and Polanyi consists

of noting that, in the London approximation,

$$\mathfrak{V}_{AB}=Q_{AB}-|V_{AB}|,$$

and similarly, for the remaining pairs, and of setting

$$Q_{AB}=(1-\kappa_{AB})\mathfrak{V}_{AB},\quad 0<\kappa_{AB}<1,$$

so that

$$|V_{AB}|=-\kappa_{AB}\mathfrak{V}_{AB},$$

where $(1-\kappa_{AB})$ is the coulombic energy fraction. Substituting these expressions (as well as similar ones for the remaining pairs of atoms) into Eq. (9), one obtains

$$\mathfrak{V}_{ABC}=(1-\kappa)(\mathfrak{V}_{AB}+\mathfrak{V}_{BC}+\mathfrak{V}_{AC})-\kappa(\mathfrak{V}_{AB}^2+\mathfrak{V}_{BC}^2+\mathfrak{V}_{AC}^2-\mathfrak{V}_{AB}\mathfrak{V}_{BC}-\mathfrak{V}_{AB}\mathfrak{V}_{AC}-\mathfrak{V}_{BC}\mathfrak{V}_{AC})^{\frac{1}{2}},$$

where, for simplicity, we have taken all the κ's equal.

For the reaction $(AB+C\rightarrow A+BC)$ the perturbation is, according to (I),

$$\mathfrak{IC}'=\mathfrak{V}_{ABC}-\mathfrak{V}_{AB}.$$

Observe that the assumed harmonic oscillator wave functions for the initial and final states effectively restrict transitions to those configurations for which the A–B and B–C distances are in the neighborhood of their equilibrium values. One may, therefore, expand $\mathfrak{IC}'$ in terms of ξ and η and neglect terms of higher order than the second. Assuming

$$\mathfrak{V}_{AB}=\mathfrak{V}_{AB}^0+\frac{h\nu_1}{2}\xi^2+0(\xi^3),$$

$$\mathfrak{V}_{BC}=\mathfrak{V}_{BC}^0+\frac{h\nu_2}{2}\eta^2+0(\eta^3),$$

one obtains

$$\mathfrak{IC}'=\mathfrak{V}_{BC}^0+\mathfrak{V}_{AC}-\kappa(\mathfrak{V}_{AB}^0+\mathfrak{V}_{BC}^0+\mathfrak{V}_{AC}+\mathfrak{V}^*)-\frac{h\nu_1}{2}\xi^2\left[1+\frac{1}{2\mathfrak{V}^*}(2\mathfrak{V}_{AB}^0-\mathfrak{V}_{BC}^0-\mathfrak{V}_{AC})\right]+\frac{h\nu_2}{2}\eta^2\left[1-\kappa-\frac{\kappa}{2\mathfrak{V}^*}(2\mathfrak{V}_{BC}^0-\mathfrak{V}_{AB}^0-\mathfrak{V}_{AC})\right],\quad(10)$$

where

$$\mathfrak{V}^*=[(\mathfrak{V}_{AB}^0)^2+(\mathfrak{V}_{BC}^0)^2+\mathfrak{V}_{AC}^2-\mathfrak{V}_{AB}^0\mathfrak{V}_{BC}^0-\mathfrak{V}_{AB}^0\mathfrak{V}_{AC}-\mathfrak{V}_{BC}^0\mathfrak{V}_{AC}]^{\frac{1}{2}}.$$

Now if the A–B and B–C distances are essentially the equilibrium values, $\mathfrak{V}_{AC}$ will depend essentially upon the angle $\measuredangle ABC$. Because we have been unable to evaluate the integrals which involve this angular dependence in any closed form, we shall crudely approximate $\mathfrak{V}^*$ by some constant value in which we assign $\mathfrak{V}_{AC}$ the value $\mathfrak{V}_{AC}^*$. In particular we shall take values for $\mathfrak{V}_{AC}^*$ in the range between that corresponding to a linear configuration, and that for which $\mathfrak{V}_{AC}$ is a minimum. Since the final results for the rate are dependent upon the actual value used for $\mathfrak{V}_{AC}^*$, they must be regarded as only approximate.[4a]

Now Eq. (10) for the perturbation may be simplified by making use of certain results of (I). It was shown there that for those transitions which have large probability the matrix elements of $(\mathfrak{V}_f-\mathfrak{V}_i)$ vanish. This permits us to eliminate the term in ξ^2 from Eq. (10). The result is that the perturbation may be taken as

$$\mathfrak{IC}'=Y_0+Y_1\eta^2,\quad(11)$$

where

$$Y_0=(\mathfrak{V}_{BC}^0+\mathfrak{V}_{AC}^*)-\kappa\left[2\mathfrak{V}_{BC}^0+\mathfrak{V}_{AC}^*+\mathfrak{V}^*-\frac{(\mathfrak{V}_{AB}^0-\mathfrak{V}_{BC}^0)(2\mathfrak{V}_{AB}^0-\mathfrak{V}_{BC}^0-\mathfrak{V}_{AC}^*)}{2\mathfrak{V}^*}\right],\quad(12a)$$

and

$$Y_1=\frac{h\nu_2}{2}\left[1-2\kappa-\frac{\kappa}{2\mathfrak{V}^*}(\mathfrak{V}_{BC}^0+\mathfrak{V}_{AB}^0-2\mathfrak{V}_{AC}^*)\right].\quad(12b)$$

For $\mathfrak{V}_{AB}^0$ and $\mathfrak{V}_{BC}^0$ nearly equal and $\mathfrak{V}_{AC}^*$ small, Y_1 is very small compared to Y_0.

Inasmuch as the quantity Y_0 is a sensitive function of κ and $\mathfrak{V}_{AC}^*$, it is impossible to obtain a value for the rate that is not subject to a degree of arbitrariness. However, this is inherent in the approximation for the potential energy of the reacting system. This unsatisfactory feature makes any agreement that is obtained between calculated and observed values of the absolute rate of questionable validity in confirming the theory.

IV. THE TRANSITION PROBABILITY

The calculation of transition probabilities requires evaluation of integrals of the sort

$$I=\int\psi_f^*\psi_i(Y_0+Y_1\eta^2)d\tau.\quad(13)$$

The probability of a transition from a particular initial to final state occurring within a time interval

[4a] Inasmuch as the actual dependence of the integrals upon the rotational state is not taken fully into account, the conclusions of sections VIII-*C*, *D* are subject to some modification. However, since the perturbation used in the present case appeared to be not very sensitive to the choices of $\mathfrak{V}_{AC}^*$ the conclusions reached there are probably not subject to marked change.

$(t_1-t_0)=t$ is given[5] by

$$P(t)=2|I|^2\left[\frac{1-\cos(\Delta Et/\hbar)}{(\Delta E)^2}\right]. \quad (14)$$

ΔE is the difference between the final and initial energies. Now, from Eqs. (6) and (13) it is readily seen that the portion of the integral I depending only upon $\mathbf{r}_2$ may be factored so that

$$I=\left[\frac{1}{V^2}\int\cdots\int\exp[(i/\hbar)\Delta\mathbf{P}\cdot\mathbf{r}_2]d\mathbf{r}_2\right]I_{int}. \quad (15)$$

Here I_{int} represents that portion of (13) integrated over the internal coordinates ξ, η, θ, θ', φ, and φ'. Carrying out the integrations in Eq. (15) and substituting in Eq. (14), we obtain

$$P(t)=\frac{16}{V^4}\left[\frac{1-\cos(\Delta Et/\hbar)}{(\Delta E)^2}\right]\times\prod_{i=x,y,z}\left[\frac{1-\cos(\Delta P_i l/\hbar)}{(\Delta P/\hbar)^2}\right]\times|I_{int}|^2, \quad (16)$$

where, for simplicity, we have taken $V=l^3$.

Since the assumed perturbation energy is independent of the angle variables θ, θ', φ, φ', the quantity I_{int} can be simplified by integrating with respect to these variables. Combining (6), (8), and (13), we see that

$$I_{int}=\frac{N_nN_m}{(a_1a_2)^{\frac{1}{2}}}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\mathcal{C}'H_n(\xi)\times\exp(-\xi^2/2)H_m(\eta)\exp(-\eta^2/2)\times Q_{KM}Q_{LN}\left(\frac{\xi}{(a_1)^{\frac{1}{2}}}+\rho_1\right)\left(\frac{\eta}{(a_2)^{\frac{1}{2}}}+\rho_2\right)d\xi d\eta,$$

where

$$Q_{KM}=\int_0^{2\pi}d\varphi\int_{-1}^{+1}d(\cos\theta)\times\exp\{(i/\hbar)(\xi/(a_1)^{\frac{1}{2}}+\rho_1)\boldsymbol{\alpha}\cdot\hat{\imath}(\theta,\varphi)\}\times P_K^{|M|}(\cos\theta)e^{iM\varphi}, \quad (17)$$

with a similar meaning for Q_{LN}. Using the value of Q_{KM} obtained in Appendix I, we have

$$|I_{int}|=\frac{16\pi^2N_nN_m\rho_1\rho_2}{(a_1a_2)^{\frac{1}{2}}}\times|P_K^{|M|}(\cos\omega_\alpha)P_L^{|N|}(\cos\omega_\beta)|\cdot|R(\alpha,\beta)|, \quad (18)$$

where ω_α, τ_α are the angle coordinates of $\boldsymbol{\alpha}$, and

$$R(\alpha,\beta)=\frac{\hbar}{8\pi\rho_1\rho_2(|\boldsymbol{\alpha}|\cdot|\boldsymbol{\beta}|)^{\frac{1}{2}}}\times\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\mathcal{C}'H_n(\xi)\exp(-\xi^2/2)H_m(\eta)\times\exp(-\eta^2/2)\left(\frac{\xi}{(a_1)^{\frac{1}{2}}}+\rho_1\right)^{\frac{1}{2}}\left(\frac{\eta}{(a_2)^{\frac{1}{2}}}+\rho_2\right)^{\frac{1}{2}}\times J_{K+\frac{1}{2}}\left(\frac{|\boldsymbol{\alpha}|}{\hbar}\left(\frac{\xi}{(a_1)^{\frac{1}{2}}}+\rho_1\right)\right)\times J_{L+\frac{1}{2}}\left(\frac{|\boldsymbol{\beta}|}{\hbar}\left(\frac{\eta}{(a_2)^{\frac{1}{2}}}+\rho_2\right)\right)d\xi d\eta. \quad (19)$$

The expression (16) must be integrated over all final translational states. It will be shown below that the number of final states having their energy and momentum in the range of specified values of these quantities and appearing in a certain element of solid angle is proportional to that element of solid angle, $d\Omega_f$, *viz.*,

$$d(\text{no. of final states})=\rho_{\Omega_f}(E_f,\mathbf{P}_f)dE_fdP_{f,x}dP_{f,y}dP_{f,z}d\Omega_f. \quad (20)$$

Following the procedure used in (I), one obtains for the probability of a chemical transition

$$\bar{P}=\int P(t)d(\text{no. of final states})=\int d\Omega_f(16\pi^4t\hbar^2/V^3)\sum_{K,M,n,\mathbf{P}_i}\exp(-E_i/kT)\times\sum_{L,N,m}\rho_{\Omega_f}(E_i,\mathbf{P}_i)|I_{int}|^2\Big/\sum_{K,M,n,\mathbf{P}_i}\exp(-E_i/kT). \quad (21)$$

The summations indicated in Eq. (21) are purely formal and are to be understood as summation over the discrete variables (i.e., K, M, etc.) and integration over the continuous variables (i.e., $\mathbf{P}_i$), for all accessible states.

V. THE DENSITY OF TRANSLATIONAL STATES

Before evaluating $\rho_{\Omega_f}(E_f,\mathbf{P}_f)$ of Eq. (20) we recall from (I) that Eq. (16) implies the conservation of energy and linear momentum. It is readily seen that the former leads to

$$\frac{|\mathbf{P}_{12}|^2}{2(m_1+m_2)}+\frac{|\mathbf{P}_3|^2}{2m_3}+\frac{\hbar^2}{2I_i}K(K+1)+(n+\tfrac{1}{2})h\nu_1+E_1=\frac{|\mathbf{P}_1|^2}{2m_1}+\frac{|\mathbf{P}_{23}|^2}{2(m_2+m_3)}+\frac{\hbar^2}{2I_f}L(L+1)+(m+\tfrac{1}{2})h\nu_2+E_2. \quad (22)$$

[5] See, for example, P. A. M. Dirac, *The Principles of Quantum Mechanics* (Oxford University Press, London, 1947), pp. 178–181. See also reference (8) of (I).

E_1 and E_2 fix the origin of vibrational energy so that zero energy corresponds to the molecule dissociated into atoms. $-(E_1+h\nu_1/2)$ is the dissociation energy of the initial molecule; similarly, $-(E_2+h\nu_2/2)$ is the dissociation energy of the final molecule. I_i and I_f are the moments of inertia of the initial and final molecule, respectively.

The conservation of linear momentum gives

$$\mathbf{P}_{12}+\mathbf{P}_3=\mathbf{P}_1+\mathbf{P}_{23}. \tag{23}$$

Equations (22) and (23), when combined, reduce to

$$\left|\mathbf{P}_1-\frac{m_1}{M}(\mathbf{P}_{12}+\mathbf{P}_3)\right|^2 = \frac{m_1(m_2+m_3)}{M^2}\left\{\left|\left(\frac{m_3}{m_1+m_2}\right)^{\frac{1}{2}}\mathbf{P}_{12} - \left(\frac{m_1+m_2}{m_3}\right)^{\frac{1}{2}}\mathbf{P}_3\right|^2 - 2\gamma M\right\},$$

where

$$M=m_1+m_2+m_3,$$

$$\gamma=(m+\tfrac{1}{2})h\nu_2-(n+\tfrac{1}{2})h\nu_1+(h^2/2I_f)L(L+1) -(h^2/2I_i)K(K+1)+(E_2-E_1). \tag{24}$$

This equation may be converted to

$$\left|\left(\frac{m_2+m_3}{m_1}\right)^{\frac{1}{2}}\mathbf{P}_1-\left(\frac{m_1}{m_2+m_3}\right)^{\frac{1}{2}}\mathbf{P}_{23}\right|^2 = \left|\left(\frac{m_3}{m_1+m_2}\right)^{\frac{1}{2}}\mathbf{P}_{12}-\left(\frac{m_3}{m_1+m_2}\right)^{\frac{1}{2}}\mathbf{P}_3\right|^2-2\gamma M. \tag{25}$$

It may be concluded from Eq. (25) that unless the initial momenta are such as to make the right side of Eq. (25) non-negative, complex values for the final momenta result. We have defined the final states by *real* values for the momenta; hence transitions for which the momenta are complex will be assigned a zero probability.

For the density of final states, we need to consider only the translational states of the system. The total number of such states may be obtained from the volume of phase space,

$$\text{no. of final states} = (1/h^6)\int\cdots\int dp_1\cdots dp_6 dq_1\cdots dq_6,$$

where p_i, q_i are conjugate variables. The p_i's represent the components of $\mathbf{P}_1$ and $\mathbf{P}_{23}$.

The integration over the position coordinates may be carried out, and the volume element in momentum space may be transformed to a new set of variables, *viz.* $(\mathbf{P}_1+\mathbf{P}_{23})$ and

$$\left[\left(\frac{m_2+m_3}{m_1}\right)^{\frac{1}{2}}\mathbf{P}_1-\left(\frac{m_1}{m_2+m_3}\right)^{\frac{1}{2}}\mathbf{P}_{23}\right]$$

instead of $\mathbf{P}_1$ and $\mathbf{P}_{23}$. One obtains

$$dp_1\cdots dp_6=d\mathbf{P}_1 d\mathbf{P}_{23} = -\frac{[m_1(m_2+m_3)]^{\frac{3}{2}}}{M^3}d(\mathbf{P}_1+\mathbf{P}_{23}) \times d\left[\left(\frac{m_2+m_3}{m_1}\right)^{\frac{1}{2}}\mathbf{P}_1-\left(\frac{m_1}{m_2+m_3}\right)^{\frac{1}{2}}\mathbf{P}_{23}\right].$$

Now we may write

$$d\left[\left(\frac{m_2+m_3}{m_1}\right)^{\frac{1}{2}}\mathbf{P}_1-\left(\frac{m_1}{m_2+m_3}\right)^{\frac{1}{2}}\mathbf{P}_{23}\right] = \frac{1}{2}\left|\left(\frac{m_2+m_3}{m_1}\right)^{\frac{1}{2}}\mathbf{P}_1-\left(\frac{m_1}{m_2+m_3}\right)^{\frac{1}{2}}\mathbf{P}_{23}\right| \times d\left[\left|\left(\frac{m_2+m_3}{m_1}\right)\mathbf{P}_1-\left(\frac{m_1}{m_2+m_3}\right)\mathbf{P}_{23}\right|^2\right]\sin u'du'dv',$$

where u', v' are the polar angles of the vector, measured with respect to some arbitrary set of space-fixed axes.

Since the integrations are to be carried out under conditions of essential conservation of momentum, we observe that the translational part of the final energy is very nearly

$$E=\frac{|\mathbf{P}_1|^2}{2m_1}+\frac{|\mathbf{P}_{23}|^2}{2(m_2+m_3)}-\frac{|\mathbf{P}_1+\mathbf{P}_{23}|^2}{2M}+\frac{|\mathbf{P}_{12}+\mathbf{P}_3|^2}{2M} = \frac{1}{2M}\left|\left(\frac{m_2+m_3}{m_1}\right)^{\frac{1}{2}}\mathbf{P}_1 - \left(\frac{m_1}{m_2+m_3}\right)^{\frac{1}{2}}\mathbf{P}_{23}\right|^2+\frac{|\mathbf{P}_{12}+\mathbf{P}_3|^2}{2M},$$

so that

$$\tfrac{1}{2}d\left\{\left|\left(\frac{m_2+m_3}{m_1}\right)\mathbf{P}_1-\left(\frac{m_1}{m_2+m_3}\right)^{\frac{1}{2}}\mathbf{P}_{23}\right|^2\right\}=MdE.$$

Combining these results, we obtain

$$d(\text{no. of final states}) = \left\{\frac{V^2}{h^6}\frac{[m_1(m_2+m_3)]^{\frac{3}{2}}}{M^2}\left(\left|\left(\frac{m_3}{m_1+m_2}\right)^{\frac{1}{2}}\mathbf{P}_{12} - \left(\frac{m_1+m_2}{m_3}\right)^{\frac{1}{2}}\mathbf{P}_3\right|^2-2\gamma M\right)^{\frac{1}{2}}\right\} \times d(\cos u')dv'd(\mathbf{P}_1+\mathbf{P}_{23})dE. \tag{26}$$

The terms in braces constitute the $\rho_{\Omega_f}(E_f, \mathbf{P}_f)$ of Eq. (20).

VI. EVALUATION OF REACTION PROBABILITY

To evaluate the probability (21), it is convenient to sum first over the quantum numbers M and N. With the use of the addition formula for spherical harmonics,[6] it can be shown that

$$\sum_{M=-K}^{K} |P_K^{|M|}(\cos\omega)|^2 = K+\tfrac{1}{2},$$

so that, from (18)

$$\sum_{M,N} |I_{int}|^2 = \frac{256\pi^4 N_n^2 N_m^2 \rho_1^2 \rho_2^2}{a_1 a_2}(K+\tfrac{1}{2})(L+\tfrac{1}{2})|R|^2.$$

Thus, (21) becomes

$$\bar{P} = \frac{1024\pi^6 h^2 \rho_1^2 \rho_2^2 t}{a_1 a_2 V^3} \frac{\int d\Omega_f \sum_{K,n,\mathbf{P}_i} N_n^2 (K+\tfrac{1}{2}) \exp(-E_i/kT) \sum_{L,m} N_m^2 (L+\tfrac{1}{2}) \rho_{\Omega_f}(E_i, \mathbf{P}_i) |R|^2}{\sum_{K,n,\mathbf{P}_i} (2K+1)\exp(-E_i/kT)}.$$

We next carry out the integration over the initial momenta, $\mathbf{P}_i$. Since

$$E_i = \frac{|\mathbf{P}_{12}|^2}{2(m_1+m_2)} + \frac{|\mathbf{P}_3|^2}{2m_3} + \frac{h^2}{2I_i}K(K+1) + (n+\tfrac{1}{2})h\nu_1 + E_1,$$

it follows that the reaction probability can be written as

$$\bar{P} = \sum_{K,L,m,n} W_{Knm}(L+\tfrac{1}{2})S, \tag{27}$$

where

$$W_{Knm} = \frac{1024\pi^6 \rho_1^2 \rho_2^2 t [m_1(m_2+m_3)]^{\frac{1}{2}} N_n^2 N_m^2 (K+\tfrac{1}{2}) \exp[-(1/kT)((h^2/2I_i)K(K+1)+nh\nu_1)]}{a_1 a_2 V h^4 M^2 \{\sum_{K,n}(2K+1)\exp[-(1/kT)((h^2/2I_i)K(K+1)+nh\nu_1)]\}}$$

and

$$S = \frac{h^6 M^2}{V^2[m_1(m_2+m_3)]^{\frac{1}{2}}} \times \int_{\Omega_f} d\Omega_f \frac{\int\cdots\int_Z \rho_{\Omega_f}(E_i, \mathbf{P}_i)|R|^2 \exp\{-(1/2kT)[(|\mathbf{P}_{12}|^2/(m_1+m_2))+(|\mathbf{P}_3|^2/m_3)]\} d\mathbf{P}_{12} d\mathbf{P}_3}{\int_{-\infty}^{\infty}\cdots\int \exp\{-(1/2kT)[(|\mathbf{P}_{12}|^2/(m_1+m_2))+(|\mathbf{P}_3|^2/m_3)]\} d\mathbf{P}_{12} d\mathbf{P}_3}.$$

In view of the discussion of Section V, the region Z in the numerator of S must be restricted to those values of $\mathbf{P}_{12}$ and $\mathbf{P}_3$ for which the final momenta are real. According to Eq. (25), Z is defined as the set of $\mathbf{P}_{12}$ and $\mathbf{P}_3$ for which

$$\left|\left(\frac{m_3}{m_1+m_2}\right)^{\frac{1}{2}}\mathbf{P}_{12} - \left(\frac{m_1+m_2}{m_3}\right)^{\frac{1}{2}}\mathbf{P}_3\right|^2 \geq 2\gamma M.$$

For the case $\gamma \leq 0$, of course, Z represents the entire space of initial momenta. To evaluate S, we introduce the following notation.

$$\mathbf{x} = \left(\frac{m_3}{m_1+m_2}\right)^{\frac{1}{2}}\mathbf{P}_{12} - \left(\frac{m_1+m_2}{m_3}\right)^{\frac{1}{2}}\mathbf{P}_3, \quad x = |\mathbf{x}|;$$

$$\mathbf{y} = \left(\frac{m_2+m_3}{m_1}\right)^{\frac{1}{2}}\mathbf{P}_1 - \left(\frac{m_1}{m_2+m_3}\right)^{\frac{1}{2}}\mathbf{P}_{23}, \quad y = |\mathbf{y}|;$$

u', v' (defined in Section V) are the polar angles of $\mathbf{y}$ with respect to some arbitrary space fixed axes; u, v are the polar angles of $\mathbf{x}$ with respect to the same axes;

σ = is the angle between $\mathbf{x}$ and $\mathbf{y}$:
$d\Omega_i = d(\cos u)dv$;
$d\Omega_f = d(\cos u')dv'$.

The following relations are easily established from (7) and (25).

$$y^2 = x^2 - 2\gamma M,$$

$$\alpha = \frac{m_1}{M}\left(\frac{m_3}{m_1+m_2}\right)^{\frac{1}{2}}\mathbf{x} - \frac{(m_1(m_2+m_3))^{\frac{1}{2}}}{M}\mathbf{y},$$

$$\beta = \frac{(m_3(m_1+m_2))^{\frac{1}{2}}}{M}\mathbf{x} - \frac{m_3}{M}\left(\frac{m_1}{m_2+m_3}\right)^{\frac{1}{2}}\mathbf{y},$$

$$\frac{|\mathbf{P}_{12}|^2}{m_1+m_2} + \frac{|\mathbf{P}_3|^2}{m_3} = \frac{1}{M}[x^2 + |\mathbf{P}_{12}+\mathbf{P}_3|^2]. \tag{28}$$

[6] E. Jahnke and F. Emde, *Tables of Functions* (Dover Publications, New York, 1945), p. 115.

These results, together with (26), suggest that the integration over initial momenta be carried out in terms of the variables $(\mathbf{P}_{12}+\mathbf{P}_3)$, x, and Ω_i. With this change of variables

$$S=\frac{h^6M^2}{V^2[m_1(m_2+m_3)]^{\frac{1}{2}}}\int_{\Omega_f}d\Omega_f\frac{\int_{\Omega_i}d\Omega_i\int_{(2\gamma M)^{\frac{1}{2}}}^{\infty}x^2\rho_{\Omega_f}(E_i,\mathbf{P}_i)\,|R|^2\exp[-x^2/(2MkT)]dx}{\int_{\Omega_i}d\Omega_i\int_0^{\infty}x^2\exp[-x^2/(2MkT)]dx},$$

where it is understood that, in the integration on x, the lower limit $(2\gamma M)^{\frac{1}{2}}$ is to be replaced by 0 when $\gamma\leqslant 0$. Using (26), we find that

$$S=\frac{1}{(2\pi MkT)^{\frac{1}{2}}}\int_{\Omega_f}d\Omega_f\int_{\Omega_i}d\Omega_i\times\int_{(2\gamma M)^{\frac{1}{2}}}^{\infty}x^2(x^2-2\gamma M)^{\frac{1}{2}}\,|R|^2\exp[-x^2/(2MkT)]dx.$$

We see from (19) and (28) that the dependence of the integrand upon Ω_i and Ω_f is due only to the appearance of $\cos\sigma$ in the quantities $|\boldsymbol{\alpha}|$ and $|\boldsymbol{\beta}|$. Since

$$\cos\sigma=\cos u\cos u'+\sin u\sin u'\cos(v-v'),$$

it is not difficult to show that

$$\int_{\Omega_f}d\Omega_f\int_{\Omega_i}F(\cos\sigma)d\Omega_i=8\pi^2\int_{-1}^{1}F(\cos\sigma)d(\cos\sigma).$$

Hence

$$S=\frac{8\pi^2}{(2\pi MkT)^{\frac{1}{2}}}\int_{-1}^{1}d(\cos\sigma)\times\int_{(2\gamma M)^{\frac{1}{2}}}^{\infty}x^2(x^2-2\gamma M)^{\frac{1}{2}}\,|R|^2\exp[-x^2/(2MkT)]dx.$$

Now, writing $\alpha=|\boldsymbol{\alpha}|$ and $\beta=|\boldsymbol{\beta}|$, it follows from (28) that

$$(\beta^2/\mu_2)-(\alpha^2/\mu_1)=2\gamma \tag{29}$$

so that $R=R(\alpha,\beta)$ can be regarded as a function of either α or β alone.

It is convenient to distinguish now between the cases $\gamma\leqslant 0$ and $\gamma>0$. For S, we shall write $S^{(-)}$ or $S^{(+)}$ according as $\gamma\leqslant 0$ or $\gamma>0$. For $\gamma\leqslant 0$, we have

$$S^{(-)}=-\frac{8\pi^2}{(2\pi MkT)^{\frac{1}{2}}}\int_{-1}^{1}d(\cos\sigma)\times\int_0^{\infty}x^2(x^2-2\gamma M)^{\frac{1}{2}}\,|R(\alpha,\beta)|^2\times\exp[-x^2/(2MkT)]dx,$$

where, according to (28),

$$\alpha=[B_1^2x^2+A_1^2(x^2-2\gamma M)-2A_1B_1x(x^2-2\gamma M)^{\frac{1}{2}}\cos\sigma]^{\frac{1}{2}},$$

$$A_1=\frac{(m_1(m_2+m_3))^{\frac{1}{2}}}{M},\quad B_1=\frac{m_1}{M}\left(\frac{m_3}{m_1+m_2}\right)^{\frac{1}{2}}.$$

We carry out the integration with respect to the variables x and α. The new volume element is

$$-\frac{\alpha d\alpha dx}{A_1B_1x(x^2-2\gamma M)^{\frac{1}{2}}},$$

and, noting that $B_1x\leqslant A_1(x^2-2\gamma M)^{\frac{1}{2}}$, we obtain

$$S^{(-)}=\frac{8\pi^2}{A_1B_1(2\pi MkT)^{\frac{1}{2}}}\int_0^{\infty}x\exp[-x^2/(2MkT)]dx\times\int_{A_1(x^2-2\gamma M)^{\frac{1}{2}}-B_1x}^{A_1(x^2-2\gamma M)^{\frac{1}{2}}+B_1x}\alpha\,|R(\alpha,\beta)|^2d\alpha.$$

Integrating first with respect to x, and using (28), we find

$$S^{(-)}=\frac{8\pi}{A_1B_1(2\pi MkT)^{\frac{1}{2}}}\times\int_{(-2\gamma\mu_1)^{\frac{1}{2}}}^{\infty}\alpha\,|R(\alpha,\beta)|^2\sinh\left\{\frac{MA_1B_1\alpha\beta}{kT\mu_1^{\frac{1}{2}}\mu_2^{\frac{1}{2}}}\right\}\times\exp\left\{-\frac{M}{2kT}\left(\frac{A_1^2\beta^2}{\mu_1\mu_2}+\frac{B_1^2\alpha^2}{\mu_1^2}\right)\right\}d\alpha. \tag{30a}$$

If we let

$$A_2=\frac{m_3}{M}\left(\frac{m_1}{m_2+m_3}\right)^{\frac{1}{2}},\quad B_2=\frac{(m_3(m_1+m_2))^{\frac{1}{2}}}{M},$$

we obtain, in an analogous fashion,

$$S^{(+)}=\frac{8\pi e^{-\gamma/kT}}{A_1B_1(2\pi MkT)^{\frac{1}{2}}}\times\int_0^{\infty}\alpha\,|R(\alpha,\beta)|^2\sinh\left\{\frac{MA_2B_2\alpha\beta}{kT\mu_1^{\frac{1}{2}}u_2^{\frac{1}{2}}}\right\}\times\exp\left\{-\frac{M}{2kT}\left(\frac{A_2^2\beta^2}{\mu_2^2}+\frac{B_2^2\alpha^2}{\mu_1\mu_2}\right)\right\}d\alpha. \tag{30b}$$

To evaluate $R(\alpha, \beta)$, let

$$\epsilon_1 = \frac{\alpha}{\hbar(a_1)^{\frac{1}{2}}}, \quad \epsilon_2 = \frac{\beta}{\hbar(a_2)^{\frac{1}{2}}},$$
$$\delta_1 = \rho_1(a_1)^{\frac{1}{2}}, \quad \delta_2 = \rho_2(a_2)^{\frac{1}{2}}. \tag{31}$$

Then, in accordance with (11) and (19),

$$R(\alpha, \beta) = R_1(\alpha) R_2(\beta)$$

where

$$R_1(\alpha) = \frac{1}{2(2\pi)^{\frac{1}{2}}\delta_1\epsilon_1^{\frac{1}{2}}} \int_{-\infty}^{\infty} H_n(\xi) \times \exp(-\xi^2/2)(\xi+\delta_1)^{\frac{1}{2}} J_{K+\frac{1}{2}}(\epsilon_1(\xi+\delta_1)) d\xi,$$

and

$$R_2(\beta) = \frac{1}{2(2\pi)^{\frac{1}{2}}\delta_2\epsilon_2^{\frac{1}{2}}} \int_{-\infty}^{\infty} (Y_0 + Y_1\eta^2) H_m(\eta) \times \exp(-\eta^2/2)(\eta+\delta_2)^{\frac{1}{2}} J_{L+\frac{1}{2}}(\epsilon_2(\eta+\delta_2)) d\eta.$$

It is clear that $R(\alpha, \beta)$ can be expressed as a simple combination of integrals of the type

$$G_{K,p} = \frac{1}{2(2\pi)^{\frac{1}{2}}\delta\epsilon^{\frac{1}{2}}} \int_{-\infty}^{\infty} (x+\delta)^{\frac{1}{2}} J_{K+\frac{1}{2}}(\epsilon(x+\delta)) x^p \times \exp(-x^2/2) dx. \tag{32}$$

Approximations to $G_{K,p}$ are obtained in Appendix II. For future reference, we note from Appendix II, that in the case $m=0$,

$$R_2(\beta) = \tfrac{1}{2} Y_0 \frac{J_{L+\frac{1}{2}}(\epsilon_2\delta_2)}{(\epsilon_2\delta_2)^{\frac{1}{2}}} \times \exp(-\epsilon_2^2/2)\left[1 - \frac{Y_1}{Y_0}(\epsilon_2^2 - 1)\right]. \tag{33}$$

With these results, and Eqs. (30a) and (30b), we see that, for a fixed set of m, n, K, L, the value of S may be obtained by numerical integration. Thus, the probability of a transition from a given initial state (n, K) to a given final state (m, L) can be calculated directly. The over-all reaction probability is then determined, in accordance with (27), by summing over all initial and final states.

For a typical reaction, values of K and L up to 10 or more must be considered, and it is clear that calculation of the reaction probability in this manner would be extremely tedious. Considerable simplification could be achieved by summing over one of the parameters K or L, but because of the dependence of γ, and hence, of the arguments of the Bessel functions, upon K and L, one could not expect, in general, to obtain closed forms for these sums. For typical reactions, however, the dependence of γ upon K and L is not very strong. Referring to Eq. (24), the quantities $\hbar^2/2I_ikT$ and $\hbar^2/2I_fkT$ are very much less than unity, and we shall be able to approximate the sum over one of the parameters, say L, by regarding γ as independent of L. We carry out this sum over the final rotational states in the next section.

VII. APPROXIMATION TO SUM OVER FINAL ROTATIONAL STATES

In summing over the final rotational states, we must distinguish between values of L for which $\gamma \leqslant 0$ and for which $\gamma > 0$. From (24), we see that if K, m, n, are chosen so that $\gamma_{L=0} > 0$, then $\gamma > 0$ for all L. If K, m, n, are chosen so that $\gamma_{L=0} \leqslant 0$, then there is an integer L_K such that $\gamma \leqslant 0$ for $L \leqslant L_K$ and $\gamma > 0$ for $L > L_K$. Accordingly, if $\sum^{(+)}$ and $\sum^{(-)}$ denote, respectively, summation over values of K, m, n, for which $\gamma_{L=0} > 0$ and $\gamma_{L=0} \leqslant 0$, we see from (27) that

$$\bar{P} = \sum_{K,m,n}^{(+)} W_{Knm} \sum_{L=0}^{\infty} (L+\tfrac{1}{2}) S^{(+)} + \sum_{K,m,n}^{(-)} W_{Knm} \left[\sum_{L=0}^{L_K} (L+\tfrac{1}{2}) S^{(-)} + \sum_{L=L_K+1}^{\infty} (L+\tfrac{1}{2}) S^{(+)} \right]. \tag{34}$$

If we assume that the dependence of γ upon L is not very strong, then L_K is usually sufficiently large so that the second term of the last series may be neglected, and the upper limit of the first term taken as $+\infty$. If, for a particular choice of K, m, n, the quantity L_K is not large, then perhaps the best procedure is to evaluate the series term by term. It is only necessary, therefore, to consider the two sums

$$\sum_{L=0}^{\infty} (L+\tfrac{1}{2}) S^{(+)}, \quad \sum_{L=0}^{\infty} (L+\tfrac{1}{2}) S^{(-)}. \tag{35}$$

In what follows, we shall suppose that $m=0$. It will be clear how the approximations can be modified for larger values of m.

From (29) and (31), it follows that

$$\epsilon_2^2 = (2\gamma h\nu_2) + (\alpha^2/\mu_1 h\nu_2), \tag{36}$$

and, using (33), Eq. (30b) becomes

$$S^{(+)} = \frac{2\pi Y_0^2 \exp[-(\gamma/kT)(1+(2kT/h\nu_2))]}{A_1 B_1 (2\pi MkT)^{\frac{1}{2}}} \times \int_0^{\infty} \frac{J_{L+\frac{1}{2}}^2(\epsilon_2\delta_2)}{\epsilon_2\delta_2} \Psi(\alpha, \beta)\, \Theta_2(\alpha, \beta) d\alpha,$$

where

$$\Psi(\alpha,\beta)=\alpha R_1^2(\alpha)\times\exp[-\alpha^2/(\mu_1 h\nu_2)]\left[1-\frac{Y_1}{Y_0}(\epsilon_2^2-1)\right]^2,$$

and

$$\Theta_j(\alpha,\beta)=\sinh\left\{\frac{MA_jB_j\alpha\beta}{kT\mu_1^{\frac{1}{2}}\mu_2^{\frac{1}{2}}}\right\}\times\exp\left\{-\frac{M}{2kT}\left(\frac{A_j^2\beta^2}{\mu_2^2}+\frac{B_j^2\alpha^2}{\mu_1\mu_2}\right)\right\},\quad j=1,2.$$

Let $c=\hbar^2/2I_f$, so that $c/kT\ll 1$. We write

$$\bar{\gamma}=\gamma-cL(L+1),$$
$$\bar{\beta}=[\beta^2-2\mu_2 cL(L+1)]^{\frac{1}{2}},$$
$$\bar{\epsilon}_2=\frac{\bar{\beta}}{h(a_2)^{\frac{1}{2}}},$$

so that $\bar{\gamma}$, $\bar{\beta}$ and $\bar{\epsilon}_2$ are independent of L. Then

$$\Theta_2(\alpha,\beta)\approx\Theta_2(\alpha,\bar{\beta})\times\exp[-(m_1m_3/Mm_2)(cL(L+1)/kT)],$$

and we have

$$S^{(+)}\approx\frac{2\pi Y_0^2\exp[-(\bar{\gamma}/kT)(1+(2kT/h\nu_2))]}{A_1B_1(2\pi MkT)^{\frac{1}{2}}}\times\int_0^\infty\Psi(\alpha,\bar{\beta})\Theta_2(\alpha,\bar{\beta})\times\left\{\frac{J_{L+\frac{1}{2}}^2(\bar{\epsilon}_2\delta_2)}{\bar{\epsilon}_2\delta_2}\exp[-\lambda L(L+1)]\right\}d\alpha,\quad(37a)$$

where

$$\lambda=\frac{c}{kT}\left[1+\frac{m_1m_3}{Mm_2}+\frac{2kT}{h\nu_2}\right].$$

Similarly, we find

$$S^{(-)}\approx\frac{2\pi Y_0^2\exp(-2\bar{\gamma}/h\nu_2)}{A_1B_1(2\pi MkT)^{\frac{1}{2}}}\times\int_{(-2\bar{\gamma}\mu_1)^{\frac{1}{2}}}^\infty\Psi(\alpha,\bar{\beta})\Theta_1\left(\alpha\left(\frac{\mu_2}{\mu_1}\right)^{\frac{1}{2}},\beta\left(\frac{\mu_2}{\mu_1}\right)^{\frac{1}{2}}\right)\times\left\{\frac{J_{L+\frac{1}{2}}^2(\bar{\epsilon}_2\delta_2)}{\bar{\epsilon}_2\delta_2}\exp[-\lambda L(L+1)]\right\}d\alpha.\quad(37b)$$

We see from (37a) and (37b) that, in order to evaluate the series (35), it will suffice to consider the series

$$\sum_{L=0}^\infty(L+\tfrac{1}{2})\frac{J_{L+\frac{1}{2}}^2(x)}{x}\exp[-\lambda L(L+1)].\quad(38)$$

(From the results of Section VI, it follows that, for $m>0$, we would encounter a linear combination of series similar to (38).)

The range of values of α which yields the bulk of the contribution to (37a) and (37b) may be extimated roughly by consideration of the maximum value of the function $\Theta_j(\alpha,\beta)$. Using (29), we find that Θ_j attains its maximum at

$$\alpha=A_j(2\bar{\gamma}\mu_1/(B_j^2-A_j^2))^{\frac{1}{2}}$$

and, from (36), that this corresponds to

$$\bar{\epsilon}_2\delta_2=B_j\delta_2\left(\frac{2\bar{\gamma}}{h\nu_2(B_j^2-A_j^2)}\right)^{\frac{1}{2}}\geqslant\delta_2\left(\frac{2|\bar{\gamma}|}{h\nu_2}\cdot\frac{m_1m_3}{Mm_2}\right)^{\frac{1}{2}}.$$

For typical reactions, this last quantity is found to be $\gg 1$, except for unusual cases in which $\bar{\gamma}$ is very near zero. This suggests that we attempt an expansion of (38) in powers of x^{-1}.

Such an expansion is obtained in Appendix III. It is shown that

$$\sum_{L=0}^\infty(L+\tfrac{1}{2})\frac{J_{L+\frac{1}{2}}^2(x)}{x}\exp[-\lambda L(L+1)]\approx\frac{1}{2\pi x^2\lambda}\left[1+\frac{1}{2x^2\lambda}\right],\quad(39)$$

provided $x^2\lambda>1$ (as is usually the case). If we combine (34), (37a), (37b) and (39), we arrive at a form for the reaction probability $\bar{P}$ that is suitable for computational purposes.

The absolute rate of reaction is then given by

$$k_f'=\bar{P}/t.$$

VIII. RESULTS AND DISCUSSION

A. The Absolute Rate

We have made use of the foregoing results to calculate the absolute rate of the reaction: $H_2+Br\rightarrow H+HBr$ at 500°K.

The calculations were carried through separately for the ortho- and para-hydrogen. In order to take into account the fact that the initial molecule in this case is homonuclear, we have multiplied the calculated rate by two. The average rate was then obtained by treating hydrogen as a mixture of 25 percent para- and 75 percent ortho-hydrogen, although no substantial differences were obtained for the absolute rates of pure ortho- and pure para-hydrogen. Molecular constants used in the calculations were taken from the paper by Hulbert and

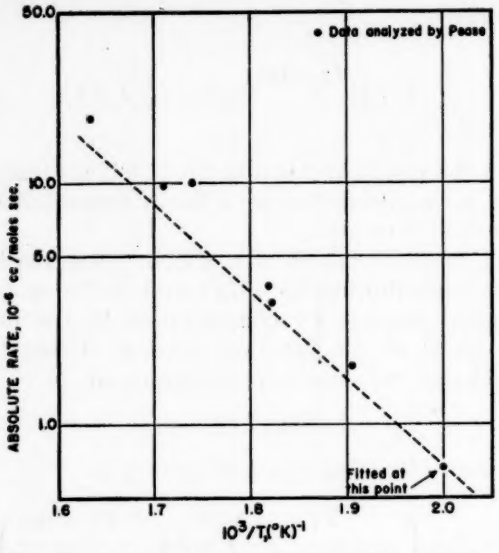

FIG. 2. Comparison of observed rates with extrapolation formula for the rate, calculated at 500°K.

Hirschfelder[7] and the complilation by Mayer and Mayer.[8]

In order to estimate the perturbation energy the quantity $\mathcal{V}_{AC}^*$ was taken between the values corresponding to a linear configuration of A–B–C and that for which $\mathcal{V}_{AC}$ is a minimum. The values for $\mathcal{V}_{AC}^*$ were calculated from the paper by Hulbert and Hirschfelder. It was found that with $\mathcal{V}_{AC}^*$ in this range of values, for a given value of κ, the absolute rate could change only by a factor of two.

The perturbation for which $\mathcal{V}_{AC}^*$ was assigned the minimum value of $\mathcal{V}_{AC}$ gave the largest value of the absolute rate, and was used in the detailed computations. The numerical value used for the perturbation was (see Eqs. (12a) and (12b)).

$$\mathcal{H}'(\text{kcal.}) = 270(\kappa - 0.67) + 3.81(1 - 1.5\kappa)\eta^2.$$

Because of the extreme sensitivity of the perturbation to the choice of κ, no value is given for the rate. Instead, Fig. 1 gives the dependence of the latter upon κ. It is seen that, with $(1-\kappa)$ ranging between 25–30 percent, agreement with experiment is obtained.

The result which has been obtained for the absolute rate is unsatisfactory because of the sensitivity of the result to the choice of κ. However, this is inherent in the Eyring-Polanyi expression used for the perturbation energy and indicates that a more accurate expression must be obtained for the potential energy of the interacting system before one can rely upon calculations of the absolute rate.

It may be noted that when $\kappa = 0.67$, $\mathcal{H}'$ vanishes. This point represents the change over from repulsive interaction between the atom and the molecule to attractive interaction. It would seem reasonable to conclude that the latter region is not attained for, otherwise one should expect to find stable molecular species (H_2Br). This emphasizes the inadequacy of the present approximation for the potential energy.

We have examined the effect of taking all κ equal (see Section III) as follows. The expressions used above were modified so that there was a κ_{H_2} and a κ_{HBr}. When the same approximations were made as for the case of equal κ's, the rate was found not to depend strongly upon κ_{H_2}. Indeed, it was found that, as κ_{H_2} varies between zero and unity, the value of κ_{HBr} needed to give agreement with experiment changes only by ten percent. Thus, the quantity κ in Fig. 1 may be identified with κ_{HBr}.

B. The Variation of Rate with Temperature

We have evaluated the quantity $RT\partial \ln k_f'/\partial T$ at 500° K. We find that in the neighborhood of this temperature the absolute rate is given by

$$k_f' = C(T)T^{-\frac{1}{2}} \exp(-17.0/RT).$$

The function $C(T)$ increases slightly with temperature. As indicated by this expression the "activation energy" is 17 kcal./mole. This may be compared with the value of 18.8 kcal./mole obtained by Pease[9] from an analysis of the data of Bodenstein and Lind and Bach, Bonhoeffer and Moelwyn-Hughes. From the rates of reaction of halogen atoms with hydrogen molecules, Morris and Pease[10] obtained a value of 17.7 kcal./mole.

In Fig. 2 we have compared the extrapolation formula obtained above with the results given by Pease[9] for the absolute rate. It is to be noted that because $C(T)$ increases with temperature, the extrapolation formula is expected to be low in the high temperature region. Nevertheless, the agreement appears to be acceptable.

C. Dependence of the Rate Upon the Initial State

Approximately 95 percent of the contribution to the rate comes from hydrogen molecules in the first excited vibrational state. The remainder is due almost exclusively to the hydrogen molecules in the ground vibrational state. The contribution from hydrogen molecules in all other vibrational states was estimated to be less than one percent. The dependence upon the vibrational and rotational state of the hydrogen molecule is presented in Fig. 3. The relative contribution to the rate was

[7] H. M. Hulbert and J. O. Hirschfelder, J. Chem. Phys. 9, 61 (1941).
[8] J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (John Wiley and Sons, Inc., New York, 1940), pp. 468–469.
[9] R. N. Pease, *Equilibrium and Kinetics of Gas Reactions* (Princeton University Press, Princeton, 1942), pp. 112–121.
[10] J. C. Morris and R. N. Pease, J. Chem. Phys. 3, 796 (1935).

calculated separately on the basis of pure ortho- or para-hydrogen, and the results are presented in a form so that the sum of the contributions for the ortho- and the para-hydrogen are each normalized to unity. For transcribing these results to the equilibrium mixture obtainable at 500°K, the values associated with para-states must be multiplied by 1/4, while the values associated with the ortho states must be multiplied by 3/4.

It is interesting to note that about 40 percent of the contribution to the rate comes from hydrogen molecules in the first excited vibrational states having rotational quantum number $K=4$. In this state, the vibrational-rotational energy of the hydrogen molecule is nearly equal to the zero-point energy of the product hydrogen bromide molecule, so that nearly all initial and final translational states are accessible. In other words, in this particular case the condition of conservation of energy puts only a slight restriction on the number of translational states that are capable of participating in transitions. It would seem, therefore, that the most important contribution to the rate is associated with those discrete states (both initial and final) which differ but slightly in energy. However, this cannot be generalized to other reactions and perturbations unless the dependence of the matrix elements on the discrete states is examined in detail.

D. Distribution of Initially Formed Products

The present formulation permits one to calculate the probability of forming hydrogen bromide in various rotational and vibrational states. It appears that much less than one percent of the hydrogen bromide is formed in any excited vibrational state. Thus we have calculated the relative probability of forming a hydrogen bromide molecule in the various rotational states, and in the ground vibrational state. Specifically, we have calculated the probabilities on the basis of hydrogen molecules having vibrational quantum number unity and rotational quantum numbers 2, 3, 4. These hydrogen molecules make up approximately 75 percent of the rate.

As indicated in Fig. 4, the distribution of hydrogen bromide among the rotational states appears to be of the form

$$\text{(number in states } L) \propto (2L+1)\exp[-(cL(L+1)/kT^*)]$$

where, however, T^* is approximately one-half the temperature of the reactants. (The distributions obtained from each of the initial rotational states gave practically the same value of T^*.) Thus it appears that if one could obtain a pure rotation spectrum of the hydrogen bromide initially formed from the reaction ($H_2+Br\rightarrow HBr+H$), an analysis of the line intensities would indicate a "temperature" of the hydrogen bromide of about 250°K compared to 500°K for the reactants. As pointed out to us by Professor Bryce L. Crawford, Jr., this distribution of rotational states may have some relation to the anomalous flame temperatures obtained from rotational spectra in flames.[11]

It may be noted that these results are suggested by Eqs. (34) and (37), which, if the integrals involved do not vary strongly with L, give the distribution formula

$$\text{(number in states } L) \sim \text{const. } (2L+1)\exp[-\lambda L(L+1)],$$

where

$$\lambda=\frac{c}{kT}\left(1+\frac{m_1m_3}{Mm_2}+\frac{2kT}{h\nu_2}\right)$$
$$\doteq 2.24(c/kT) \quad \text{at} \quad T=500°\text{K}.$$

From this distribution one would expect a value of 222°K for T^*.

IX. REMARKS

The results of this study show that the London-Erying-Polanyi expression taken for the potential energy is a sensitive function of the coulombic

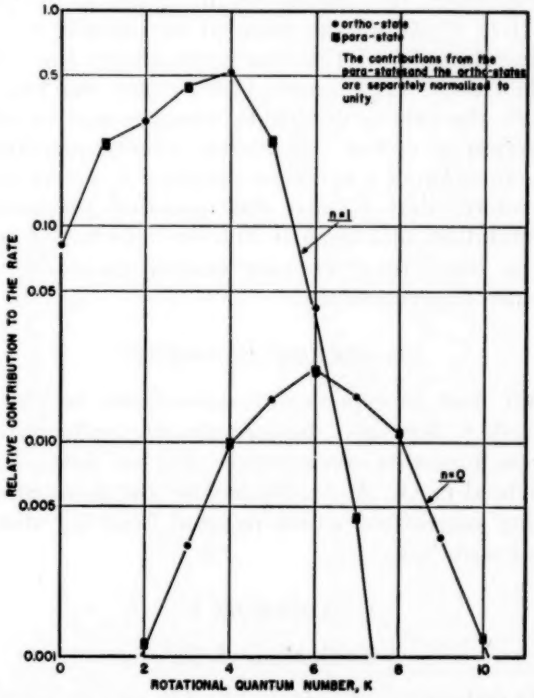

FIG. 3. Contribution to the rate by H_2 molecules in various vibrational and rotational rates.

[11] See, for example, A. G. Gaydon and H. G. Wolfhard, Proc. Roy. Soc. **A194**, 169 (1948).

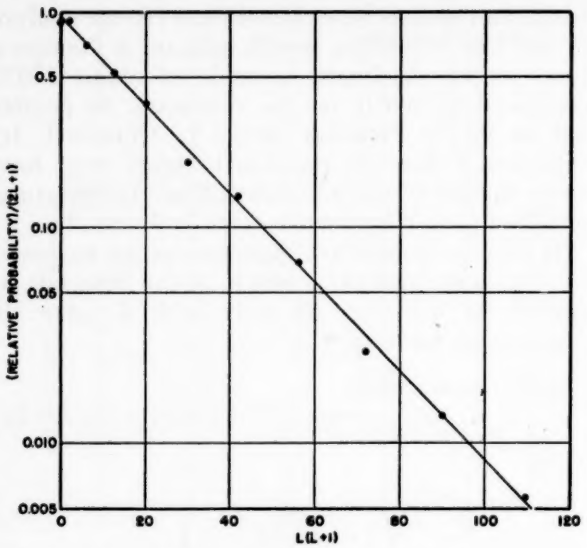

FIG. 4. Distribution of initially formed HBr among rotational states. The "temperature" calculated from the slope is 253°K.

energy fraction, $(1-\kappa)$. Consequently the absolute rate may not be calculated, from this approximation, without a great deal of uncertainty. Before any confidence can be had in computed values of the absolute rate, it seems clear that a more exact expression for the potential energy of interacting systems is needed.

However, the *relative* results given in Sections VIII-*B*, *C*, *D* are not affected appreciably by the value chose for κ. This can be seen from Eqs. (11), (12a), and (12b); since $Y_0 \gg Y_1$ (for the present case), the rate is essentially proportional to some function of κ. For the relative results mentioned, this function of κ no longer appears. It would seem, therefore, that to test the quantum mechanical formulation of chemical kinetics which has been given here, these relative results should be examined experimentally.

X. ACKNOWLEDGMENTS

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APPENDIX I

Evaluation of Q_{KM}

To evaluate Q_{KM} defined by Eq. (17), we note first that, by definition, $\hat{\imath}$ is a unit vector along the internuclear axis of the initial molecule, so that $\boldsymbol{\alpha}\cdot\hat{\imath}$ represents the projection of $\boldsymbol{\alpha}$ upon that axis. Therefore

$$\exp[(i/\hbar)(\xi/(a_1)^{\frac{1}{2}}+\rho_1)\boldsymbol{\alpha}\cdot\hat{\imath}(\theta,\varphi)]=\exp(i\delta_0\cos\zeta),$$

where

$$\delta_0=(|\boldsymbol{\alpha}|/\hbar)(\xi/(a_1)^{\frac{1}{2}}+\rho_1),$$

and

ζ is the angle between $\boldsymbol{\alpha}$ and $\hat{\imath}$.

From the addition theorem for Bessel functions,[12] we obtain

$$\exp(i\delta_0\cos\zeta)=(2\pi/\delta_0)^{\frac{1}{2}}\sum_{n=0}^{\infty}(n+\tfrac{1}{2})i^nJ_{n+\frac{1}{2}}(\delta_0)P_n(\cos\zeta),$$

where J_n represents a Bessel function of the first kind and P_n a Legendre function of the first kind. From the addition theorem of spherical harmonics,[6] it can be shown that

$$P_n(\cos\zeta)=\frac{2}{2n+1}\sum_{m=-n}^{n}P_n^m(\cos\theta)P_n^m(\cos\omega_\alpha)\exp[im(\varphi-\tau_\alpha)],$$

where θ, φ are the angle coordinates of $\hat{\imath}$, ω_α, τ_α are the angle coordinates of $\boldsymbol{\alpha}$, both referred to the same set of space fixed axes.

Substituting these results into Eq. (17) and carrying out the integrations, one obtains, by means of the orthogonality properties of the functions involved,

$$Q_{KM}=(2\pi/\delta_0)^{\frac{1}{2}}i^KJ_{K+\frac{1}{2}}(\delta_0)P_K^{|M|}(\cos\omega_\alpha)\exp(iM\tau_\alpha).$$

APPENDIX II

Evaluation of $G_{K,p}$

In order to approximate $G_{K,p}$ defined by Eq. (32), we note that, in the cases of interest, $\delta\gg1$, so that, because of the factor $\exp(-x^2/2)$, the bulk of the contribution to the integrand comes from values of x considerably less than δ. Writing[13]

$$(\epsilon(x+\delta))^{\frac{1}{2}}J_{K+\frac{1}{2}}(\epsilon(x+\delta))=P(\epsilon(x+\delta))\sin\epsilon(x+\delta)+Q(\epsilon(x+\delta))\cos\epsilon(x+\delta),$$

where $P(x)$ and $Q(x)$ are polynomials in x^{-1}, we have, for these values of x,

$$(\epsilon(x+\delta))^{\frac{1}{2}}J_{K+\frac{1}{2}}(\epsilon(x+\delta))\approx P(\epsilon\delta)\sin\epsilon(x+\delta)+Q(\epsilon\delta)\cos\epsilon(x+\delta),$$

so that

$$G_{K,p}\approx\frac{1}{2(2\pi)^{\frac{1}{2}}\delta\epsilon}\Big[P(\epsilon\delta)\int_{-\infty}^{\infty}x^p\sin\epsilon(x+\delta)\exp(-x^2/2)dx+Q(\epsilon\delta)\int_{-\infty}^{\infty}x^p\cos\epsilon(x+\delta)\exp(-x^2/2)dx\Big].$$

But, if we write

$$\Phi_1(x)=\frac{1}{(2\pi)^{\frac{1}{2}}}\exp(-x^2/2),\quad \Phi_p(x)=\frac{d^{p-1}}{dx^{p-1}}\Phi_1(x),$$

it is not difficult to show that

$$\frac{1}{2\pi}\int_{-\infty}^{\infty}\begin{matrix}\sin\\\cos\end{matrix}(\epsilon(x+\delta))x^{2p}\exp(-x^2/2)dx=(-1)^p\Phi_{2p+1}(\epsilon)\begin{matrix}\sin\\\cos\end{matrix}(\epsilon\delta).$$

Thus

$$G_{K,2p}\approx\frac{(-1)^p(\pi)^{\frac{1}{2}}}{\sqrt{2}\delta\epsilon}\Phi_{2p+1}(\epsilon)[P(\epsilon\delta)\sin\epsilon\delta+Q(\epsilon\delta)\cos\epsilon\delta]=(-1)^p\Phi_{2p+1}(\epsilon)\left(\frac{\pi}{2\epsilon\delta}\right)^{\frac{1}{2}}J_{K+\frac{1}{2}}(\epsilon\delta).$$

Estimates of $G_{K,2p+1}$ may be obtained by integration by parts. For example, since

$$\frac{d}{dx}\{x^{\frac{1}{2}}J_{K+\frac{1}{2}}(x)\}=(K+1)x^{-\frac{1}{2}}J_{K+\frac{1}{2}}(x)-x^{\frac{1}{2}}J_{K+3/2}(x),$$

it follows that

$$G_{K,1}=\frac{K+1}{2(2\pi)^{\frac{1}{2}}}\int_{-\infty}^{\infty}\frac{J_{K+\frac{1}{2}}(\epsilon(x+\delta))}{(\epsilon(x+\delta))^{\frac{1}{2}}}\exp(-x^2/2)dx-\epsilon G_{K+1,0}.$$

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[12] G. N. Watson, *Theory of Bessel Functions* (Cambridge University Press, London, 1945), p. 368.

[13] See reference 12, pp. 52–53.

The first integral here can be approximated by a procedure analogous to that used above, and we find

$$G_{K,1}\approx\Phi_1(\epsilon)\left[\frac{K+1}{\delta}\left(\frac{\pi}{2\epsilon\delta}\right)^{\frac{1}{2}}J_{K+\frac{1}{2}}(\epsilon\delta)-\epsilon\left(\frac{\pi}{2\epsilon\delta}\right)^{\frac{1}{2}}J_{K+3/2}(\epsilon\delta)\right].$$

Approximations for $G_{K,3}$, $G_{K,5}$... are obtained in a similar manner.

APPENDIX III

Evaluation of Series of Bessel Functions

We obtain here an asymptotic expansion of the series

$$\sum_{L=0}^{\infty}(L+\tfrac{1}{2})\frac{J_{L+\frac{1}{2}}^2(x)}{x}\exp[-\lambda L(L+1)], \tag{38}$$

in powers of x^{-1}. We suppose $x\gg1$, $\lambda\ll1$ and $x^2\lambda>1$. From the definition[13] of $J_{L+\frac{1}{2}}(x)$, it is easy to show that

$$J_{L+\frac{1}{2}}^2(x)=\frac{2}{\pi x}\left[\sin^2\left(x-\frac{L\pi}{2}\right)+\frac{L(L+1)}{x}\sin(2x-L\pi)+\frac{L^2(L+1)^2}{4x^2}\cos^2\left(x-\frac{L\pi}{2}\right)-\frac{(L+2)(L+1)L(L-1)}{4x^2}\sin^2\left(x-\frac{L\pi}{2}\right)+0(x^{-3})\right],$$

so that, if we let

$$Q'=\sum_{L\text{ even}}(L+\tfrac{1}{2})\exp[-\lambda L(L+1)],$$

$$Q''=\sum_{L\text{ odd}}(L+\tfrac{1}{2})\exp[-\lambda L(L+1)],$$

we have

$$\sum_{L=0}^{\infty}(L+\tfrac{1}{2})\frac{J_{L+\frac{1}{2}}^2(x)}{x}\exp[-\lambda L(L+1)]=\frac{2}{\pi x^2}\left[Q'\sin^2x+Q''\cos^2x+\frac{\sin2x}{x}\left(\frac{dQ'}{d\lambda}-\frac{dQ''}{d\lambda}\right)+\frac{1}{4x^2}\left\{\left(\frac{d^2Q'}{d\lambda^2}-\frac{d^2Q''}{d\lambda^2}\right)\cos2x-2\sin^2x\frac{dQ'}{d\lambda}-2\cos^2x\frac{dQ''}{d\lambda}\right\}+0(x^{-3})\right].$$

Now, for small λ

$$Q'\approx Q''\approx\tfrac{1}{2}\sum_{L=0}^{\infty}(L+\tfrac{1}{2})\exp[-\lambda L(L+1)]\approx\frac{1}{4\lambda},$$

and

$$\frac{dQ'}{d\lambda}\approx\frac{dQ''}{d\lambda}\approx-\frac{1}{4\lambda^2},\quad\frac{d^2Q'}{d\lambda^2}\approx\frac{d^2Q''}{d\lambda^2},$$

so that

$$\sum_{L=0}^{\infty}(L+\tfrac{1}{2})\frac{J_{L+\frac{1}{2}}^2(x)}{x}\exp[-\lambda L(L+1)]\approx\frac{1}{2\pi x^2\lambda}\left[1+\frac{1}{2x^2\lambda}\right].$$

Higher order terms may be obtained, if necessary, by the same procedure.

The Fermi Gas Model Applied to the Thermal Electromotive Forces of Tin, Lead, and Indium

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The absolute thermoelectric powers of tin, lead, and indium in the temperature range of 2–10°K are taken from data of Keesom and Matthijs. The temperature dependence of thermal e.m.f. is parabolic, as predicted for a Fermi gas. With an additional assumption regarding a mean free path parameter (i.e., $d(\log l)/d\epsilon \ll 1$), the Fermi energies for tin, lead, and indium are calculated to be 5.72, 2.89, and 1.20 ev, respectively. Low temperature specific heat data then provide an estimate of the number of conduction electrons per atom. The latter values are 2.54, 2.39, and 0.50, respectively.

INTRODUCTION

BORELIUS[1] has calculated the absolute thermoelectric power for tin from measurements of thermoelectric power of a tin-lead thermocouple at temperatures below the superconducting threshold of lead. These calculations depend upon the conclusion that the Thomson coefficient, σ, and hence the thermoelectric power, $(d\phi/dT)$, of a superconductor are very small or zero. Recently Daunt and Mendelssohn[2] have verified this conclusion by a direct measurement of σ. Consequently, the validity of using a thermocouple composed of a superconductor and a non-superconductor to study the absolute thermoelectric behavior of the non-superconductor is substantiated.

Keesom and Matthijs[3] have made more accurate measurements of the e.m.f.'s of the thermocouples tin-lead and indium-lead at liquid helium temperatures. Casimir and Rademakers[4] experimented over a narrow temperature interval with a thermocouple of tin-lead. In both cases the primary intent was apparently to ascertain the thermoelectric behavior of the superconductor and investigate the possible "announcement" of superconductivity at temperatures just above the transition temperature. In view of the increased accuracy, it is of some interest to review these data to determine the thermoelectric behavior of the non-superconductor. In particular, the data of Keesom and Matthijs[3] allow a comparison of the thermoelectric properties of normal tin, lead, and indium with those predicted for a Fermi gas. In this model, the triply periodic potential within the metal is replaced by an average potential, and the electronic interactions are neglected. Agreement over even a small temperature range at low temperatures might ultimately aid in the understanding of thermoelectric phenomena in spite of the obvious over-all inadequacy of this model.

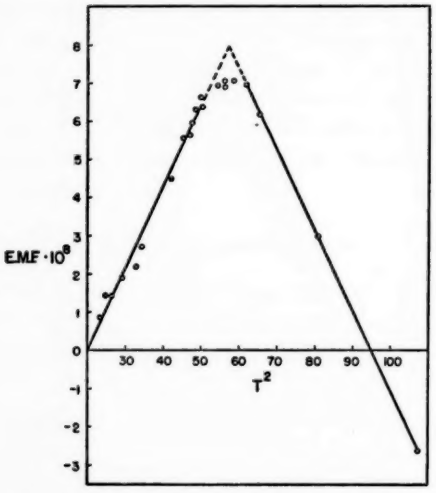

FIG. 1. Thermal e.m.f. *versus* T^2 for Sn-Pb thermocouple; $T_0^2(\text{Sn}) = 52.71$; $T_0^2(\text{Pb}) = 13.62$; $T_1^2 = 17.81$; T_0 = superconducting threshold temperature; T_1 = temperature of cold junction.

THEORETICAL

Latimer[5] has expressed the thermoelectric power in terms of the Thomson coefficients of the two metals which make up the thermocouple:

$$e(d\phi/dT) = \int_0^T \sigma_N(T)(dT/T) - \int_0^T \sigma_{SC}(T)(dT/T). \quad (1)$$

With the Thomson coefficient for the superconducting metal, σ_{SC}, equal to zero, Eq. (1) expresses the absolute thermoelectric power of the normal metal. It may be applied to any theory of metals which predicts the functional form of $\sigma_N(T)$. For example, the Maxwell-Boltzmann collision equation applied to a Fermi gas yields an expression for σ in terms of the Fermi energy, μ_0,[6] which can be con-

[1] G. Massing, *Handbuch der Metallphysik* 1.1, 396 (1935).
[2] J. G. Daunt and K. Mendelssohn, Proc. Roy. Soc. (London) **A185**, 225 (1946).
[3] W. H. Keesom and C. J. Matthijs, Physica **5**, 1 (1938).
[4] H. B. G. Casimir and A. Rademakers, Physica **13**, 33 (1947).
[5] W. M. Latimer, J. Am. Chem. Soc. **44**, 36 (1922).
[6] E.g., see F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940).

veniently expressed in terms of the Sommerfeld heat capacity. Substitution into Eq. (1) yields

$$e(d\phi/dT) = -(2\gamma T/3) - (k^2\pi^2/3) \times [l'(\epsilon)/l(\epsilon)]_{\epsilon=\mu_0} \cdot T, \quad (2)$$

in which $\phi(T)$ = electrical potential, $l(\epsilon)$ = mean free path of electron of energy ϵ, $l'(\epsilon) = dl/d\epsilon$, and $\gamma T = (\pi^2 k^2 T/2\mu_0)$ = Sommerfeld heat capacity.

Since thermal e.m.f. is actually measured rather than thermoelectric power, the integrated form of Eq. (2) is more convenient for comparison with data.

$$e[\phi(T_2) - \phi(T_1)] = -(\gamma/3)(T_2^2 - T_1^2) - (k^2\pi^2/3)\int_{T_1}^{T_2} [l'(\epsilon)/l(\epsilon)]_{\epsilon=\mu_0} \cdot T dT. \quad (3)$$

Equation (3) predicts a parabolic temperature dependence if either of the two conditions below is satisfied:

(a) $[l'(\epsilon)/l(\epsilon)]_{\epsilon=\mu_0} \cdot \mu_0 \ll 1$ i.e., the last term of (2) is negligible.

(b) $[l'(\epsilon)/l(\epsilon)]_{\epsilon=\mu_0}$ is not a function of temperature.

TEST OF THE THEORY

A qualitative test of Eq. (3) is obtained by investigating the linearity of a plot of measured e.m.f. against the square of the temperature of the variable junction. It is to be noted that the parabolic temperature dependence should also be applicable in the temperature range where neither metal is superconducting. Figures 1 and 2 show the plots of thermal e.m.f. *versus* T^2 for tin-lead and for indium-lead, respectively. The data were taken from reference 3.

Equations (4), (5), (7), and (8) were obtained from Figs. 1 and 2 by the method of least squares. Equation (6) is the difference between Eqs. (4) and (5), and its slope, in the region $T^2 = 60$ to $T^2 = 110$, is determined by the thermoelectric power of lead alone.

$$\text{Sn-Pb}(sc) = +0.213 \cdot 10^{-8}(T^2 - 20.0) \text{ volts } 4.8 < T < 7.1°\text{K}, \quad (4)$$

$$\text{Sn-Pb} = -0.210 \cdot 10^{-8}(T^2 - 95.0) \text{ volts } 7.4 < T < 10.4°\text{K}, \quad (5)$$

$$(4)-(5) = +0.423 \cdot 10^{-8}(T^2 - 57.7) \text{ volts } 7.4 < T < 10.4°\text{K}, \quad (6)$$

$$\text{In-Pb}(sc) = +0.99 \cdot 10^{-8}(T^2 - 15.0) \text{ volts } 4.0 < T < 5.7°\text{K}, \quad (7)$$

$$\text{In-Pb}(sc) = +1.04 \cdot 10^{-8}(T^2 - 18.3) \text{ volts } 4.2 < T < 6.9°\text{K}. \quad (8)$$

It is of interest to note that the e.m.f. of indium is indicated in reference 3 with opposite sign to that of tin. In a later paper[7] these same authors specify that the thermoelectric currents for indium and tin are in the same direction and in agreement with the expected direction. Consequently, this sign discrepancy has been ignored. The lowest point in the low temperature indium data and the four lowest points for lead have been omitted in the least squares calculations. These deviations from the parabolic

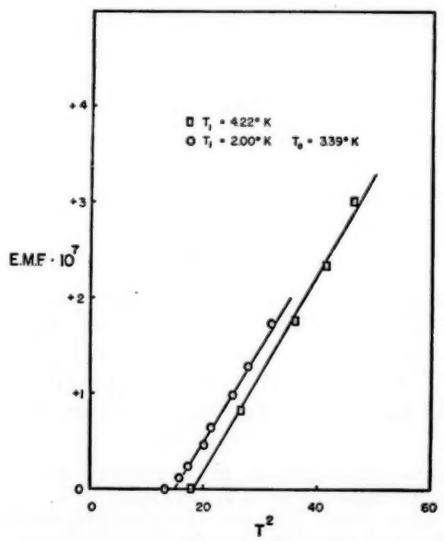

FIG. 2. Thermal e.m.f. *versus* T^2 for In-Pb thermocouple; $T_0^2(\text{In}) = 11.36$; $T_0^2(\text{Pb}) = 13.62$.

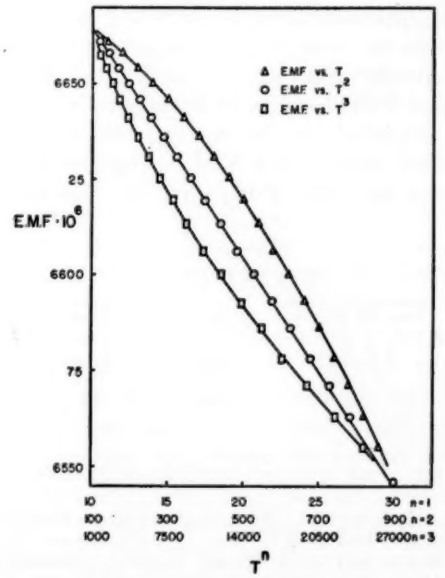

FIG. 3. Thermal e.m.f. *versus* T, T^2, T^3 for copper-constantan thermocouple.

[7] W. H. Keesom and C. J. Matthijs, Physica **5**, 443 (1938).

TABLE I.

Metals	μ_0 from thermal e.m.f.	μ_0 from electron diffraction work function	μ_0 from Fermi gas
Tin	5.72 ev	—	10.19 ev
Lead	2.89	7±3 ev	9.45
Indium	1.20	—	8.67

temperature dependence are observed only immediately before the onset of superconductivity and are presumed to correspond to the previously mentioned "announcement" of superconductivity.[4]

If a parabolic temperature dependence applies to absolute thermoelectric power, it should also apply to the relative thermoelectric power obtained from a normal non-superconducting thermocouple. The data of Giauque, Johnston, and Kelley[8] for the copper-constantan thermocouple offer sufficient accuracy to give a test of this conclusion. Figure 3 shows the smooth curve e.m.f. values listed by Giauque *et al.*, plotted against T, T^2, and T^3 for the same temperature interval. It is evident that significant curvature is present in a T or T^3 plot while the T^2 plot is linear at least as high as 22°K.

Evidently the data of Keesom and Matthijs, as well as that of Giauque, Johnston, and Kelley, are compatible with a simple parabolic temperature dependence at low temperatures. Further test of the applicability of the Fermi gas approximation is not possible without a decision as to which of the requirements, (a) or (b), is satisfied by (l'/l). Mayer and Mayer[9] indicate that the second term in (3) is expected to be negligible, i.e., condition (a) is applicable, whereas Seitz[6] does not make this assumption. Wilson[10] finds the assumption of Mayer and Mayer valid at moderate temperatures and uses it as a first approximation at very low temperatures. The parabolic temperature dependence indicates experimentally that either condition (a) or (b) must be satisfied if the Fermi gas model can be applied. It will be assumed herein, in agreement with both Wilson and Mayer and Mayer, that condition (a) determines the form of Eq. (3). The validity of the further test of the Fermi gas model is conditional on this assumption.

Equation (3) allows calculation of the Sommerfeld heat capacity per mole of electrons, γT, and consequently the Fermi energy, μ_0, from the slopes of the least squares curves. The values of μ_0 are compared in Table I to the "theoretical" values obtained by assuming that the number of electrons equals the classical valence and that the entire atomic volume is accessible to them. One independent experimental measurement of μ_0 is available from the measurements of work function, w, and the inner potential, u,[11] by use of the equation:

$$\mu_0 = u - w.$$

Rupp[12] has measured the inner potential for lead by means of the index of refraction for slow electrons and finds 11±3 ev. The inner potentials for tin and indium are not available. The work function for lead, determined by the photoelectric effect,[13,14] is 4.1 ev. As mentioned above, the heat capacity per mole of electrons may be calculated. Consequently, a knowledge of the actual electronic specific heat allows a calculation of the number of electrons per atom. This estimate is still subject to the approximations of the Fermi gas but requires no assumptions concerning the volume accessible to these electrons. The electronic specific heats of tin, lead, and indium have been obtained either by calorimetric measurements followed by subtraction of the lattice specific heat or by superconducting threshold field measurements.[15] These specific heats and the corresponding number of electrons per atom are given in Table II. For comparison, Table II includes the values of N obtained by Keesom and Matthijs.[7] These are based on the application of Gorter's cycle to a partially superconducting thermocouple in a magnetic field. The equation derived on this basis does not precisely represent the dependence of ϕ upon H, as shown by a lack of constancy of N as the field is varied, but the order of magnitude is probably reliable. Also, the number of bonding orbitals given by Pauling and Ewing[16] is shown.

TABLE II.

Metals	Electronic atomic heat cal./deg. $\cdot 10^4$	N	N Mattijs and Keesom	N Pauling and Ewing
Tin	3.5–4.0[a, b]	2.54	1.9–3.5	2.53
Lead	7.0[16]	2.39	7.0	2.53
Indium	3.5[16]	0.50	0.6	3.53

[a] J. A. Kok, Physica **1**, 1103 (1933–4).
[b] W. H. Keesom and P. H. von Laer, Physica **5**, 193 (1938).

DISCUSSION

Thermal e.m.f. at very low temperatures varies with the square of the temperature of the variable junction within the experimental error of the data available. Since this is the temperature dependence predicted for a Fermi gas, quantitative calculations

[8] W. F. Giauque, H. L. Johnston, and K. K. Kelley, J. Am. Chem. Soc. **49**, 2367 (1927).
[9] J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (John Wiley and Sons, Inc., New York, 1937), p. 413.
[10] A. H. Wilson, *Theory of Metals* (Cambridge University Press, London 1936), p. 208.
[11] H. Bethe, Ann. d. Physik **87**, 55 (1928).
[12] E. Rupp, Ann. d. Physik **1**, 773 (1929).
[13] A. Hughes, Trans. Roy. Soc. (London) **312**, 205 (1912).
[14] R. Hamer, J. Opt. Soc. Am. **A9**, 251 (1924).
[15] J. G. Daunt, A. Horseman, and K. Mendelssohn, Phil. Mag. **27**, 754 (1939).
[16] L. Pauling and F. J. Ewing, Rev. Mod. Phys. **20**, 112 (1948).

based on this model and the experimentally obtained "absolute thermoelectric power" were made. The resulting estimates of the Fermi energy, μ_0, were found to be of the same order of magnitude as the calculated values for tin, lead, and indium. Together with experimentally measured electronic specific heats, these values of μ_0 allow calculation of the number of electrons per atom. The numbers obtained are of the correct order of magnitude and for tin and lead are in apparent agreement with those predicted by Pauling.

The thermoelectric properties of a metal are probably concerned with only a fraction of the metallic electrons, those of highest energy. The apparent applicability of the Fermi gas theory suggests that the energy levels occupied by these electrons in this temperature range have the Fermi gas character (e.g., density of energy levels) even though the over-all energy level scheme may not. Hence measurements of "absolute thermoelectric power" may well be useful in calculation of other properties of this same group of electrons. In addition, the estimate of the number of conduction electrons per atom is potentially of considerable aid in the formulation of a theory of metallic binding.

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The Hot Atom Chemistry of the Propyl Bromides*,†

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The chemical effects of the recoil from the capture gamma-radiation produced by the (n, γ) reaction on bromine 81 in both normal and isopropyl bromides have been investigated. It is found that the principal part of the radiobromine resisting aqueous extraction, that is, organically combined, is propyl bromide. The ratio of normal to isopropyl bromide formed by irradiation of either normal or isopropyl bromide is found to be about 2.5. The irradiation of propyl bromide cooled to liquid nitrogen temperatures produced no change in the yield of normal and isopropyl radiobromides as compared with the results for the liquids at room temperature. In direct contrast, however, the yield of the dibromides requiring hydrogen substitution was much larger in the case of the low temperature solid, the percentage yield of dibrom rising about fourfold. These results are interpreted as evidence that the bromine substitution is a reaction occurring largely in the high energy range where the chemical bonds involved are negligible, and that the hydrogen substitution occurs in the lower energy range where the recoiling bromine atoms collide with the molecule as a whole in an inelastic manner rather than with a single atom, as is postulated in the high energy range. The difference in temperature dependence of the two types of substitution reaction would appear to arise from the difference in magnitude of the energies involved. The fact that the irradiation of isopropyl bromide produces 2.4 times as much normal bromide as iso bromide and the same relative amounts are observed in the irradiation of normal propyl bromide is taken as further evidence of the extremely energetic nature of the bromine substitution reaction, the free radical apparently having sufficient energy to isomerize before recombination occurs in the solvent "cage."

I. INTRODUCTION

THE capture of a slow neutron by bromine 81 to form 34-hour bromine 82 involves the emission of the order of 8 million volts energy as gamma-radiation nearly instantaneously. It is not known whether this energy is emitted in the form of one gamma-ray or whether there are several involved. If one is involved the recoiling bromine will possess an energy of about 420 electron volts. If a cascading process occurs the recoil energy will vary between this limit and zero, the chance of zero recoil energy being extremely small unless a very large number of gamma-rays are involved in the cascade. It is well known that the radiobromine atoms are ejected from the molecules in which they resided before the neutron capture,[1–6] the evidence being that the irradiation of a liquid organic halide allows about half of the radiohalide to be extracted into an aqueous solution,[1,2,4] and that the irradiation of a gaseous organic halide allows the extraction of over 95 percent,[3,5,6] and that the irradiation of a dilute solution of an organic halide in an organic solvent reduces the fraction of the radiohalide found in the mother molecule to zero as the concentration is decreased.[2,4] The mechanism by which the radio-

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[1] L. Szilard and T. A. Chalmers, Nature **134**, 462 (1934).
[2] E. Gluckauf and J. W. J. Fay, J. Chem. Soc. 390 (1936).
[3] Hans Suess, Zeits. f. physik. Chemie **B45**, 297 (1939).
[4] W. F. Libby, J. Am. Chem. Soc. **62**, 1930 (1940).
[5] W. F. Libby, Science **93**, 283 (1941).
[6] S. Wexler and T. H. Davies, unpublished private communication.

TABLE I. Principal data on propyl bromide.

	25°	−196°	1 g Br_2/100 cc
Isopropyl retentions			
Iso	10.0	11.2	7.9
Normal	23.7	23.5	2.6
1,2 Dibrom	3.8	20.0	6.7
1,3 Dibrom	4.6	11.5	4.8
R	42.1	66.0	21.4
Normal propyl retentions			
Iso	12.0	11.3	4.0
Normal	30.6	28.5	9.0
1,2 Dibrom	3.8	20.2	8.4
1,3 Dibrom	4.5	18.2	5.4
R	50.0	78.2	28.8

active halogen atoms are reincorporated into organic molecules may be of considerable interest both in radiochemistry and indirectly in chemical kinetics. It has been proposed[4, 5, 7] that the broad features of this type of reaction can be explained by a mechanism which considers the chemical bonds to be of strength negligible with respect to the energy of the recoiling bromine atom and that the re-entry process consists of an essentially head-on collision of the recoiling bromine atom with a bound bromine atom, the radioactive bromine atom transferring its momentum nearly completely to the inactive atom and being itself left with a relatively small energy in the immediate vicinity of the free radical formed by the removal of the non-radioactive atom, both the free radical and the radiobromine atom being contained in the same solvent "cage"[8] and being free to recombine, with a dissipation of their excess energy to the solvent through the cage.

Substitution for hydrogen atoms in an organic halide has been explained as occurring near the end of the range of the recoiling bromine atom where the energy is still somewhat larger than the chemical bond energy but not a great deal larger; that is, the energy is sufficient to cause bond rupture but is insufficient to warrant treatment of the collision as a process occurring essentially between free atoms. This allows the molecule as a whole to act in an inelastic manner to stop the radiobromine atom in the same solvent "cage" and to itself dissociate, for example, by losing a hydrogen atom, the whole process resulting in a replacement of hydrogen by bromine to form a more highly halogenated product. This type of process can be dominant apparently when the medium contains a very low concentration of either combined or free halogen, as Reid[9] has shown by studying very dilute solutions of iodine in pentane and establishing that 38 percent of the radioiodine appears as amyl iodide. This result has been confirmed in this laboratory by Mr. W. H. Johnston, who found 37 percent under similar conditions and observed that no significant decrease in iodine titre occurred. A similar experiment with 0.10 g of Br_2 in 100 cc of liquid pentane was performed and a retention of 31 percent observed. The yields of hydrogen substitution products reported in the literature for the organic halides in general are considerably less than this, though they vary with experimental conditions, as we shall see later in this paper. It appears therefore to be necessary to explain the increase in effectiveness of the hydrogen substitution reaction with diminution in halogen concentration. Such an explanation seems to follow from the collisional type of theory referred to above. According to this theory hydrogen entry can occur only for those halogen atoms which possess an energy between one and several times the bond energy. If there are no halogen atoms in the solution, energy loss occurs entirely by collisions with much lighter atoms so that *every halogen atom will move through this critical energy range*, thereby having an opportunity to substitute by the inelastic molecular collision mechanism described. If, however, an appreciable fraction of the cooling collisions occur with atoms of equal mass the chance of the atoms *jumping discontinuously through this energy interval* is appreciable and the result is a considerable fraction of the atoms will have no opportunity for hydrogen substitution. The whole problem is analogous to that of resonance capture in neutron physics.

In addition to these processes in the hot or high energy range and in the chemical bond energy range, which we might call "epithermal" in analogy to the neutron nomenclature, we may have reactions proceeding in the thermal range between the solution and those halogen atoms which do manage to enter the thermal range without chemical combination, i.e., halogen atoms are notoriously reactive and the possibilities of their combining with impurities, walls, and the principal species in the solution may be considerable, and care must be taken in work in the field of hot atom chemistry to guard against misinterpreting such phenomena as occurring in the hot or epithermal ranges. A further type of reaction which is not characteristic of or to be attributed directly to the hot or epithermal chemistry is the type of reaction discovered by Sugden,[10] in which the addition of small amounts of aniline to an organic halide greatly reduced the retention in organic forms. This has been interpreted[4, 5, 7] as a reaction between the excited, reformed organic halide and aniline present in the solution in such concentrations as to have a good chance of collision with the excited organic halide

[7] W. F. Libby, J. Am. Chem. Soc. 69, 2523 (1947).
[8] J. Franck and E. Rabinowitch, Trans. Faraday Soc. 30, 120 (1934).
[9] A. F. Reid Phys. Rev. 69, 530 (1946).
[10] C. S. Lu and S. Sugden, J. Chem. Soc. 1273 (1939).

before it cools. It is to be expected that this type of reaction will be found to be quite common. Fortunately, the result generally can be predicted by experiments with macroscopic quantities. For example, the ability of aniline to react with organic halides to form *N*-substituted anilinium salts in which the halogen is ionically bound is well known. This reaction is known to occur at elevated temperatures in ordinary organic systems. In addition, a third type of essentially thermal reaction which must be borne in mind in the interpretation of experiments on hot atom chemistry is thermal exchange reactions between halogen atoms and organic halides. It is probable that in most cases studied so far this effect has been negligible, but it is not unlikely that in certain cases, for example the benzyl or allyl halides, this effect will be serious.

The present research was undertaken to elucidate some of the doubtful points in the theoretical structure described above. The 34-hour bromine activity was selected because of its convenient half life, and the availability and stability of the organic bromides. The propyl bromides were selected from the various organic bromides for the ease of separation of the products by distillation techniques, at the same time retaining the possibility of isomerization.

II. EXPERIMENTAL

Pure normal propyl bromide and isopropyl bromide samples were obtained from Paragon Testing Laboratory. These were redistilled and their refractive indices found to check with those for the pure products within 1 part per ten thousand. The irradiations were conducted in 500 cc soft glass bottles near the cyclotron target with an intervening 10 cm of paraffin for neutron moderation and 2 inches of lead to eliminate radiochemical effects caused by gamma-radiation. Exposures usually lasted one hour, at a mean flux of about 10^8 thermal neutrons per square centimeter per second. The beam current on the cyclotron usually averaged 20 microamperes. A beryllium target was used. The bottle was approximately 18 inches from the target. After exposure, the samples were returned immediately to the chemical laboratory and extracted within 5 minutes with aqueous sulfite containing bromide carrier, after which 25 cc of the irradiated liquid was mixed with 25 cc of the mono brom isomer, 25 cc of the 1,2-dibrom propane, and 25 cc of the 1,3 dibrom propane. The distillation was conducted by taking middle cuts of 10 cc for each of the 4 constituents. The 1,1 and 2,2-dibrom propanes were not added because they were not available. Apparently they were not formed in any appreciable yield because the material balance obtained for the radiobromine in the four cuts listed accounted within the accuracy for the entire radiobromine content of the organic fraction left after the aqueous extraction.

TABLE II. Supplementary data on propyl bromide retentions.

A. Effect of added Br_2 on retention; isopropyl bromide

Concentration (g/100 cc)	3.5	1.0	0.35	0.035
Retention (%)	22.7	21.4	26.5	39.4

B. Effect of standing in dim light 24 hours after irradiation; normal propyl bromide with 0.7 g Br_2/100 cc

	Immediate (1.0 g Br_2)	24-hr. delay (0.7 g Br_2)
Iso	4.0	6.5
Normal	9.0	10.3
1,2 Dibrom	8.4	17.8*
1,3 Dibrom	5.4	8.2
R	28.8	42.8

C. Effects of excluding air and of continuous extraction during irradiation; normal propyl bromide

	Usual procedure	Air excluded	Cont. extraction
Iso	12.0	9.7	—
Normal	30.6	29.7	—
1,2 Dibrom	3.8	3.8	—
1,3 Dibrom	4.5	6.8	—
R	50.0	51.0	50.0

* Macroscopic yield of about 1 percent 1,2 dibrompropane corresponding to observed loss in Br_2 titre was observed.

The boiling points of the 1,1 and 2,2 compounds probably are sufficiently different to insure their not being included in the center cuts for the four compounds used. The radioactivity measurements were made with a standard type of liquid cell counter, 10 cc of liquid being measured. Precautions were taken to allow the 18-minute and 4.5-hour bromine activities to decay and a lead shield of 2-mm thickness was used as a combination absorber of the 18-minute radiation and radiator for the 34-hour gamma-radiation for those experiments where the decay period was insufficient. Measurement of the rate of decay of the radioactivity showed it to be essentially pure 34 hour. Table I presents the major portion of the experimental results.

The upper half of the table refers to experiments in which isopropyl bromide was irradiated and the lower half to those belonging to normal propyl bromide. The second column gives the percentages of the total 34-hour radiobromine found in the various chemical forms indicated by the designations in the first column. The last row in each half of the table refers to the total retention in organic form as experimentally observed after the aqueous extraction, the symbol *R* being used. The third column of the table contains the data for the experiments in which the exposure was made at liquid nitrogen temperatures. In general, the data in the table are accurate to about ± 1 unit, e.g., the isopropyl fraction found in normal propyl irradiations at room temperature would be 12.0 ± 1.

In addition some study was made of the effect of concentration of added bromine on total organic retention in the case of isopropyl bromide. The numbers are given in Table II. From these data it is

seen that the effect of added bromine is essentially saturated at 1 gram per 100 cc and has essentially disappeared at 0.035 gram per 100 cc. The fourth column of Table I contains the detailed retention data for this concentration. Checks on loss of titre of elemental bromine were made and very little loss of titre occurred during the course of the experiment.

It was necessary to extract the irradiated halides immediately after exposure in order to avoid a very considerable increase in the observed retention. For example, allowing a solution irradiated at room temperature to stand over night would result in retentions of about 80 percent, and in a rather irreproducible fashion, and it was discovered that reproducibility could be obtained only by immediate extraction after relatively short exposure. To test the efficacy of our adopted procedure one experiment was performed in which extraction occurred continuously throughout the irradiation. The organic and aqueous layers were placed together in a sealed glass tube which was rotated with a motor end over end throughout the exposure. Normal propyl bromide was used and the observed total organic retention was 50.0 percent, in good agreement with that observed at the end of one hour of exposure and a 5-minute extraction interval, the bromide carrier in the aqueous layer being less than 0.1 percent of the total bromine in the system. The retention in this case was measured by comparing the activities in the aqueous layer with that in the organic layer in contrast to our usual procedure of counting the liquid before and after aqueous extraction. The thought occurred to us that the addition of Br_2 might well stabilize the system, it being considered possible that the slow growth in retention was due to the reaction of unusual species such as atomic bromine with impurities in the system. An experiment was performed with normal propyl bromide in which 0.7 gram of elementary bromine per 100 cc was added. The irradiation was conducted and the solution allowed to stand in a dimly lit room for 24 hours, nearly the same conditions of illumination being used as had obtained throughout the research. The result was an increase in retention from 28.8 percent to 42.8 percent with a sharp increase in the 1,2 dibrom yield. A loss in titre of the Br_2 and a macroscopically observable yield of 1,2 dibrom propane as indicated by a refractive index measurement was found. The total distribution data are given in Table II. This experience led to the thought that the slow thermal rise in retention might involve the presence of air in the solutions as well as the illumination, so an experiment was performed in which air was carefully excluded, other conditions being unchanged from the standard procedure. These and other data supplementary to Table I are given in Table II, and it is clear that the exclusion of oxygen had no effect within experimental error.

Experiments were performed with various amounts of lead shielding and with a 0.5-gram radium-beryllium source, instead of the cyclotron, which show the retention pattern to be independent of radiation intensity. We take this as evidence that secondary reactions with free radicals generated by gamma-rays or fast neutrons were negligible.

III. DISCUSSION

The type of explanation previously proposed for hot atom phenomena and referred to above in the Introduction appears to be capable of explaining many of the data obtained in this research.

1. *The temperature independence of the yields of mono brom derivatives.* The data in Table I reveal that the yield of mono brom products is independent of the temperature during exposure in sharp contrast to the dibrom derivatives. To recapitulate, the explanation of the predominance of the reactions leading to the reformation of the bombarded molecule in the hot atom chemistry of organic compounds, particularly the organic halides, has been that the recoiling halogen atom while still in the hot range, that is, possessing an energy several times the chemical bond energy, makes a nearly head-on collision with bound bromine in an organic halide molecule, driving the inactive bromine onwards with a transfer of momentum to it and leaving the radioactive bromine atom in the same solvent cage with the free radical so produced. In our case this free radical would be propyl radical and the radiobromine would be expected to recombine with the propyl radical to form a mono brom derivative. It seems that the efficacy of the cage in this high energy range must be a matter mainly of the density of solvent molecules in the cage walls rather than of any adhesive forces operating between them, for the reason that the residual energy of the bromine atom probably is large compared to any such binding energy. A rough theoretical calculation[7] of the bromine atom energies involved indicates that these are of the order of $\frac{1}{2}$ to $\frac{2}{3}$ the chemical bond energy, which is large with respect to the intermolecular adhesive energies. Therefore, the only temperature effect one might expect in this range is a slight difference in molecular density. The re-entry to form the mono brom derivatives leaves the bromine so energetic on the average that the question of whether it is reflected from the walls is not connected with the question of how tightly the wall particles are held to one another but is a matter of reflection of the bromine on the individual wall molecules. These collisions probably are somewhat inelastic, the cooling of the bromine atom occurring partially through molecular excitation of the wall molecules. After the cooling has proceeded to a cer-

tain point, recombination occurs, a certain number of collisions with the wall having preceded the recombination. The freshly reformed molecule is excited and then it in turn cools by wall collisions.

2. *The formation of both the normal and isopropyl isomers in ratio of 2.4 to 1 from both normal and isopropyl mother molecules.* The data reveal that the ratio of the yields of normal and isopropyl bromide is nearly the same for both normal and isopropyl bromide bombardments, the average value being 2.4 ± 0.2, and there being some slight indication that the ratio for iso is slightly less than that for the normal, as though there were indeed some slight tendency to form that isomer identical with the mother molecule—a certain memory for the configuration existing before the hot atom collision.

The explanation proposed for this observation is that during the period of existence of the free radical, that is, the interval between the initial collision forming the free radical and the instant of recombination after the cooling period for the energetic radiobromine atom, the propyl radical itself is free to isomerize essentially to the equilibrium state it would have at extremely high temperatures. It is thought probable that the propyl radical itself will receive considerable excitation energy in the rupturing collision forming it from the propyl bromide, and that this energy of excitation will be so high as to promote free isomerization so that the radical retains very little memory of its original configuration when formed, and that when recombination does occur the final product will reflect only slightly the nature of the original radical. Some slight memory is found due to those few cases where essentially immediate recombination occurs because the bromine was left relatively cool by virtue of a chance almost exactly head-on collision. It would seem that the truly high temperature distribution ought to be 3 to 1, since there are 6 methyl hydrogen and 2 methylene hydrogen positions. The fact that it is 2.4 to 1 instead and that there is evidently some remembrance of the nature of the mother molecule probably have the same explanation.

3. *The yield of the dibrom derivatives is much larger for the solids at liquid nitrogen temperature than for the liquids at room temperature.* Table I shows further that the yields of the hydrogen substitution products increase three- to fivefold on cooling, in sharp contrast to those for the halogen substitution products, the only exception being the 1,3 dibrom formed from isopropyl for which the factor is 2.5 *versus* about 5 for 1,2 from isopropyl and both 1,2 and 1,3 from normal propyl.

It has been proposed that hydrogen substitution in an organic halide is brought about by the halogen atom colliding with the molecule as a whole with an energy which we have termed epithermal, and defined as being above the bond energy but not extremely large as compared to it, amounting perhaps to twice the bond energy, though this limit is rather indefinite. The essential point is that as the halogen atom reaches the end of its range the collisions become less a matter of collision with individual atoms in the molecule and more a matter of inelastic collisions with the molecule as a whole or groups thereof, until the thermal range is reached when truly elastic collisions with the molecule as a whole occur. In the epithermal region the molecule is able to stop the bromine atom in the same solvent cage and due to its high degree of internal excitation shed hydrogen and bromine atoms and whole radicals.*** With this model one notices that the residual energy of the bromine is very likely to be much less than in the case described above where the mono brom derivatives are formed, and that therefore any change in the adhesive energies and densities of packing of the molecules constituting the cage wall will be more important. The greater dependence on density and strength of the cage wall in the case of these lower energy atoms can perhaps be seen best in the following way. In the higher energy case the bromine has sufficient energy to melt or vaporize the whole cage in any case. It matters little therefore in this case whether one starts from a solid or from a liquid, but in the case of the epithermal processes this probably is not true and so the strength of the cage and its general efficacy will depend considerably on whether the cage is compact and more tightly bound as in the low temperature solid or whether it is more attenuated and less tightly bound as in the liquid. Further experiments must be performed at intermediate temperatures to settle whether the density, i.e., the phase, is more important than the mean temperature. It seems not unlikely that if one cools through the melting point a rather abrupt change in the yield of the dibrom derivatives may occur.

The observation that the increase in yield of 1,3 dibrom product from isopropyl bromide at liquid nitrogen temperatures is less than for the 1,2 and also for 1,2 and 1,3 yields for the normal propyl bromide appears to be a definite result. One notices that the formation of the 1,3 product from the isopropyl requires a very considerable shuffling of the atoms in the molecule and particularly that the carbon-bromine bond on the central carbon atom must be broken. This requirement does not occur for the other three cases, of the 1,2 from the

*** Some evidence has been obtained for this type of phenomenon in another research on the hot atom chemistry of dilute bromine solutions in pentane where a small yield of propyl bromide has been observed, amounting to some 4 percent of the total bromine activity where the total organic retention was 40 percent. It must be said, however, that no evidence in the course of the research on propyl bromide has appeared for the formation of such products as 1 or 2 carbon alkyl bromides.

isopropyl and the 1,2 and 1,3 from the normal propyl. With this observation in mind, an obvious explanation seems to be that this shuffling process can occur only for the most energetic of the collisions and that a good fraction of them do not possess sufficient energy to allow it. It might also be taken as evidence that the actual process involved in a good fraction of the cases is not only the ejection of a hydrogen atom but also of the bound bromine atom, and that then one has an inactive bromine atom, the radioactive bromine atom, and the propylene di radical all loose in the cage and recombination of these three constitutes the last step of the reaction.

4. *The lower retention in isopropyl as compared to normal propyl irradiations.* It is clear from Table I also that the total organic retention in the isopropyl case appears to be definitely less than for the normal propyl case, and that this ratio apparently is independent of temperature, both temperatures giving the value of 1.2 for the ratio of the retentions.

The most obvious explanation of this observation is that the bromine is somewhat more shielded by the methyl radical in isopropyl bromide than by the ethyl radical in normal propyl bromide. Examination of Fischer-Hirschfelder models seems to bear this out.

5. *The presence of bromine in the irradiated organic bromide greatly reduces the total retention, the main decrease occurring in the mono brom derivatives.* Tables I and II show that the addition of bromine greatly reduces the total retention, the main reduction occurring in the primary products with some increase in the hydrogen substitution occurring.

The explanation proposed for this is that of exchange occurring during the cooling process either before or after the reformation of the molecule, the re-formed molecule being more highly excited in the case of the primary products. It is well known that all organic halides exchange at sufficiently high temperatures with either the halogen or the halide ion, the activation energies being 18.12K cal./mole for normal propyl and 22.94 for isopropyl against bromide ion.[11] The exchange between bromine atom and Br_2 is of course extremely rapid, so we have the interesting possibility that if the concentration of bromine is sufficiently high so that each solvent cage contains a bromine molecule or that a bromine molecule be within one or two layers of the solvent cage one might expect the radioactivity to be "washed out" into the Br_2 and so made water extractible with a consequent reduction in the overall retention. It seems that exchange of the bromine atom must proceed only with a bromine molecule in the solvent cage itself, in other words, occur only at the high bromine concentrations, but that the reformed organic bromide may retain some of its energy of excitation for a sufficiently long time to be able to exchange with the Br_2 within one or two layers of the solvent cage. It is interesting to observe in Table II that the effect seems to be saturated at about 0.5 gram of organic bromide per 100 cc of propyl bromide.

6. *The inversion by the presence of bromine during irradiation of the usual ratio of normal to isopropyl products in the case of isopropyl bromide.* The indications are that the usual ratio of normal to iso products is unchanged in the case of normal propyl bromide irradiations by the addition of bromine, but it is indeed inverted in the case of isopropyl bromide.

The explanation of this point is not clear. It is possible that the lower activation energies of the exchange reaction for the normal product is involved, it being remembered that to form the normal from the iso requires that the free radical isomerize and therefore that more energetic processes be involved than in the direct formation of the iso.

7. *The delayed rise in retention.* The observed increase in retention from about 50 percent to nearly 80 percent on standing for 24 hours in a dimly lit room at room temperature is probably connected with photochemical or oxygen promoted chain brominations of the alkyl halide itself. It is possible that the effect is due to impurities in the alkyl halides and reactions of either atomic bromine or Br_2 or HBr with these. This type of effect has been reported previously and is rather widely recognized by workers in hot atom chemistry. It is quite clear from these results that one must be careful in working with 34-hour bromine and weak neutron sources to eliminate this effect occurring during long exposure. By using the cyclotron it was possible to obtain sufficient intensity with short exposures.

The authors would like to express their indebtedness to Professors Kharasch and Urry of the Chemistry Department for extensive discussions of organic chemical problems involved in this research.

[11] G. A. Elliott and S. Sugden, J. Chem. Soc. 1836 (1939).

The Properties of 86-Second $I^{(136)}$*

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A short-lived iodine which was discovered by Strassmann and Hahn as a U fission product was shown to have a half-life of 86±1 seconds. It emits 6.5-Mev beta-rays and 2.9-Mev gamma-rays. The fission yields in U^{235}, Pu^{239}, and U^{233} are 3.1 percent, 1.9 percent, and 1.7 percent, respectively. A mass assignment to 136 has been shown to be the most likely one. The observed 86-sec. I activity does not originate from a Te parent whose half-life is greater than 20 seconds.

INTRODUCTION

STRASSMANN and Hahn in 1940 discovered[1] a short-lived iodine with a half-life of 1.8±0.4 minutes which they extracted from neutron irradiated uranium. Seelmann-Eggebert and H. J. Born[2] showed that this iodine does not decay to an active xenon whose half-life is between several hours and about half a minute. Snell and co-workers[3] confirmed the existence of the isotope as a fission product of uranium and reported a half-life of about 1.5 minutes. During an investigation by Katcoff, Miskel, and Stanley[4] of the ranges of fission recoils from plutonium, an attempt was made to detect this iodine but it could not be found under the conditions of the experiment. It seemed at the time that one cause for this failure might be an abnormally low fission yield from plutonium. Therefore a detailed investigation was made.

EXPERIMENTAL METHOD

The uranium or plutonium was irradiated at the center of the homogenous pile (water boiler) at Los Alamos for periods of one, two, or three minutes. Carrier was added and iodine was then extracted, usually[5] by the radiochemical method of Glendenin and Metcalf.[6] This consists of an oxidation of the iodine with NaOCl in basic solution to insure exchange, reduction to free I_2, extraction with CCl_4, reduction to I^-, re-oxidation to I_2, extraction with more CCl_4, reduction to I^- again, and finally precipitation as AgI. However, in these experiments an additional oxidation-extraction-reduction cycle was introduced. The AgI samples were mounted on flat cards and placed opposite the mica window of a bell-type Geiger counter. Measurements were usually begun about 4 minutes after the end of bombardment except in the final yield determinations when the time was about 6 minutes. The scaling circuit had a variable scale which could be varied from a scale of 64 to a scale of 2. Readings were taken every 20 seconds for about the first 10 minutes, and thereafter once every minute. As the counting rate decreased the recorder was switched to lower scales so that it was unnecessary to read the interpolation lights. Counting was interrupted for 5 seconds each time a change of scale was made.

HALF-LIFE

The first four decay curves were taken with no added absorber. These indicated a half-life of 85±3 seconds. Each curve had a longer-lived tail which was due mostly to 54-min. I and 6.7-hr. I. It was later found that the amount of this tail could be greatly reduced by counting through 513 mg/cm² of aluminum absorber. Therefore three decay curves were taken under these conditions and only these runs were used for the half-life determination (Fig. 1). This was calculated by means of the formula

$$T_{\frac{1}{2}} = (0.693t/\ln R)$$

where $T_{\frac{1}{2}}$ is the half-life, R is the ratio of total counts from zero to infinity to the total counts from time t to infinity, where t is so chosen that R is about 5. The number of counts after 8 half-lives of decay was calculated since there were no experimental points beyond this on the decay curve of the short-lived iodine after the long-lived tail was subtracted. The calculated number of counts was a small fraction of the total and therefore any error introduced by an incorrect choice of half-life for the calculation is entirely negligible. The values obtained were 86.8, 84.7, and 86.6 seconds. A graphical analysis of the same curves yielded values of 86.2, 84.3 and 85.0 seconds, respectively. The final result is taken as 86±1 seconds.

* A summary of this paper was presented at the 113th meeting of the American Chemical Society held in Chicago during April 1948.
** Now at Brookhaven National Laboratory, Upton, L. I., N. Y.
[1] F. Strassmann and O. Hahn, Naturwiss. **28**, 817 (1940).
[2] W. Seelmann-Eggebert, and H. J. Born, Naturwiss. **31**, 59 (1943).
[3] A. H. Snell and co-workers, Manhattan Project Report, CP-1011 p. 4, October 25, 1943.
[4] S. Katcoff, J. A. Miskel, and C. W. Stanley, Phys. Rev. **74**, 631 (1948).
[5] See section on fission yield below for the alternative method.
[6] L. E. Glendenin and R. P. Metcalf, Manhattan Project Report, CN-1312, p. 55, March 15, 1945; Plutonium Project Record IX B, 8.21.2 (1946).

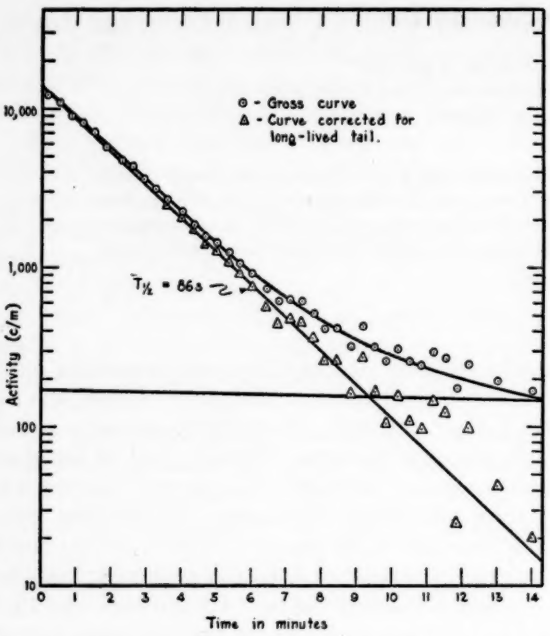

FIG. 1. Decay curve of 86-sec. I through 513 mg Al/cm².

BETA-RAY ENERGY

The beta-ray energy of the 86-sec. I was found by taking an absorption curve in aluminum. The sample was placed on the third shelf and the absorbers were placed above it, on the second shelf for the first part of the curve and directly above the sample for the latter part of the curve. Decay curves through three absorbers were followed for each run, as the absorbers could be added or removed in about one-half second, a time short compared to the 20-second counting intervals. In each run one point of the previous run was repeated, so all runs could be normalized to the first one. The amount of uranium irradiated was adjusted for each bombardment so that the initial count of each decay curve was between 5000 c/m and 10,000 c/m. The absorption curve (Fig. 2) was obtained by plotting the 86-sec. I activity, as read from the resolved decay curves at five minutes after the end of each bombardment (an isochron), against the thickness of aluminum. An end point of 3400 mg Al/cm² was obtained by a Feather analysis of the absorption curve. This corresponds to a maximum beta-energy of 6.5 Mev, using the relationship between the range and the energy of beta-particles given by Glendenin.[7] The validity of this relationship was tested for the known 5.0-Mev beta-rays of 37-min. Cl^{38}. The measured range in Al agreed with the predicted value[7] well within the experimental error of about 10 percent. The error was this large because 1.1-Mev and 2.8-Mev beta-rays are also emitted by Cl^{38}. The 86-sec. I absorption curve seems to indicate a single component, although another, somewhat softer component, if present, would be masked by the harder one.

[7] L. E. Glendenin, Nucleonics 2, 12 (1948).

GAMMA-RAY ENERGY

An absorption curve in lead of the 86-sec. I was taken in nearly the same manner as the absorption curve in aluminum. One lead absorber was placed next to the window of the counting tube and the others were placed under it, as close to it as possible. The sample was on the fourth shelf. The amount of uranium bombarded was varied to give an initial count of 5000 c/m to 10,000 c/m for each run. The absorption curve was obtained from an isochron taken through the resolved decay curves at five minutes after the end of each bombardment. The curve (Fig. 3) shows a gamma-ray with a half-

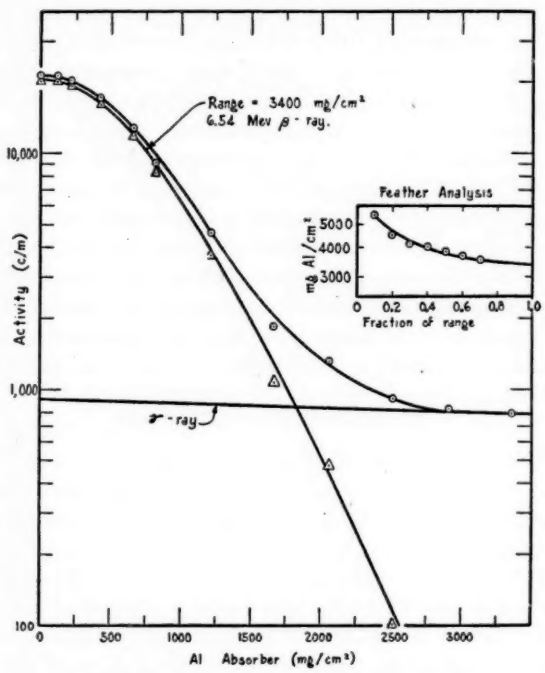

FIG. 2. Absorption curve in Al of 86-sec. iodine.

thickness of 19.6 g Pb/cm². This corresponds to an energy of 2.9 Mev as read from an unpublished plot of gamma-ray energy against half-thickness in lead for a similar experimental arrangement. To check this curve, the absorption in lead of the gamma-rays emitted by a sample containing ThC, ThC′, and ThC″, was measured with the same apparatus under the same conditions. A half-thickness in Pb of 18.3 g/cm² was obtained which is caused almost entirely by the 2.62-Mev gamma-ray of ThC″. The curve gives a half-thickness of 18.6 g/cm² for this gamma-ray. In a study of hard gammas in gross fission products by Spatz, Hughes, and Cahn[8] a

[8] W. D. B. Spatz, D. J. Hughes, and A. Cahn, Manhattan Project Declassified Report MDDC-871 (April 1946).

2.65-Mev gamma-ray is reported for a 90-sec. period. The 86-sec. I undoubtedly contributes to this, although there may be one or more other fission products of about the same half-life which also have hard gammas, as the intensity they found was rather high.

FISSION YIELD

The fission yield of the 86-sec. I was measured in natural uranium, Pu^{239}, and U^{233} after irradiation with mainly slow neutrons in two series of experiments. In each case the yield was determined relative to that of 85-min. Ba^{139}. The yield of the latter in U^{233} was interpolated from the data of Steinberg *et al.*,[9] as 6.0 percent.

In the first series of experiments, a *solution* of each fissionable isotope was irradiated in the pile. The sample was removed at the end of bombardment and shaken to insure homogeneity. Iodine carrier equivalent to 60.0 mg of AgI was added to an aliquot and a radiochemical analysis for iodine was performed. Counting was continued for about 15 minutes. Then the sample was dried, dismounted quantitatively, and weighed. The remaining solution was allowed to stand until the 18-min. Ba^{141} had decayed to a negligible amount. Two aliquots, each containing five times the volume taken for the iodine analysis, were then removed and analyzed radiochemically for barium.[10] The results are given in Table I. Corrections were made for the degree of saturation produced during the bombardment and, in the case of Ba^{139}, for absorption of the beta-rays and for the 7-min. Cs parent. The average values of the fission yields from U^{235}, Pu^{239}, and U^{233} were 2.3 percent, 1.1 percent, and 1.2 percent, respectively.

TABLE I. Fission yields of 86-sec. I as determined from fissionable isotopes irradiated in aqueous solution.

U^{235} Run	U^{235} Yield (percent)	Pu^{239} Run	Pu^{239} Yield (percent)	U^{233} Run	U^{233} Yield (percent)
1	2.2	3	1.2	5	1.3
2	2.4	4	1.1	6	1.1
Average	2.3	Average	1.1	Average	1.2

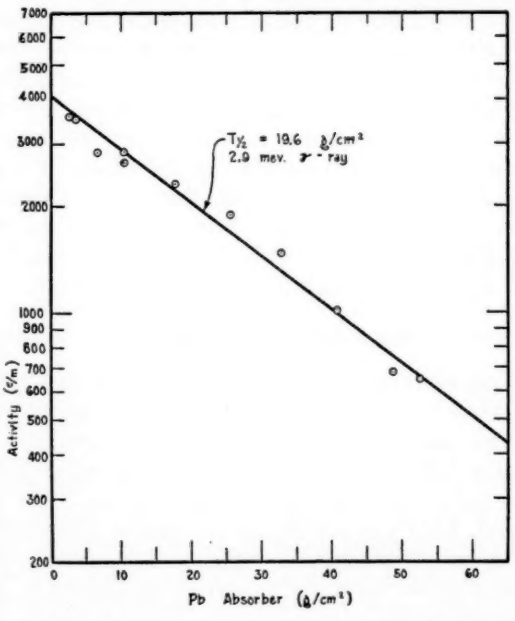

FIG. 3. Absorption curve in Pb of 86-sec. iodine.

In view of these low values as compared with the total chain yields of about 6 percent predicted by the yield-mass curves,[9] another series of experiments was performed. The chemical procedure described above may have been performed too rapidly to allow for complete exchange of the radioactive iodine with the carrier iodine. Therefore the procedure was modified by irradiating the fissionable material in a metallic medium so that the fission product iodine would presumably all be in the iodide state which exchanges instantaneously with iodide carrier. The normal uranium was irradiated as the metal surrounded with aluminum foil. The Pu^{239} and U^{233} were evaporated from solution onto aluminum foils. The size of the deposit was so small that virtually all of the fission recoils were stopped in the aluminum. Immediately after a short irradiation (1.0 or 3.0 minutes) the metal and fission recoils were dissolved in warm HCl containing iodide and Ba^{++} carriers. Then a small excess of $KMnO_4$ was added followed by enough hydroxylamine hydrochloride to reduce the iodate to free iodine. This was extracted with CCl_4, reduced to iodide and then two more oxidation-extraction-reduction cycles were performed as in the first procedure.[11] The samples of AgI were counted and weighed as before but in several of the runs a rough determination was also made of the fission yield of 6.7-hr. I^{135}. In these cases it was necessary to dismount and dissolve the AgI periodically so that the 9.2-hr. Xe^{135} daughter could be boiled away.[11] Only three decay points, spaced a few hours apart, were obtained for 6.7-hr. I in these runs. The fission yield values found for the 6.7-hr. I could be compared with previously reported values and thus serve as an indication of the completeness of exchange achieved in these experiments. The aqueous phases remaining after the first CCl_4 extractions were used for the 85-min. Ba analyses.

The data used in the fission yield calculations are

[9] E. P. Steinberg, J. A. Seiler, A. Goldstein, and A. Dudley, A.E.C. declassified document MDDC-1632 (Nov. 1, 1947); also "Nuclei formed in fission," J. Am. Chem. Soc. **68**, 2411 (1946).

[10] Concentrated HCl procedure adapted from L. E. Glendenin, Plutonium Project Record IX B, 8.23.1 (1946).

[11] This method is a modification of a procedure used previously to measure the U^{238} fission yield of 6.7-hr. I. S. Katcoff, C. R. Dillard, H. Finkelstein, B. Finkle, J. A. Seiler, and N. Sugarman, Plutonium Project Record IXB, 7.33.3 (1946).

TABLE II. Data used in calculation of fission yield of 86-sec. I from U^{235} irradiated in a metallic medium.

Run	Isotope analyzed	Chemical yield (percent)	Activity corr. for decay and chem. yield (c/m)	Corr. for saturation	Corrected saturation activity (c/m)	Fission yield (percent)
7	86-sec. I	35.3	4.90×10^5	1.307	6.40×10^5	3.2
	85-min. Ba	31.1	3.15×10^4	41.4	12.5×10^5	(6.3)
	6.7-hr. I					
8	86-sec. I	43.3	4.21×10^5	1.307	5.50×10^5	2.4
	85-min. Ba	52.1	3.69×10^4	41.4	14.6×10^5	(6.3)
	6.7-hr. I		6250	193.4	13.3×10^5	5.7
9	86-sec. I	21.0	3.52×10^5	1.307	4.59×10^5	3.2
	85-min. Ba	44.7	2.28×10^4	41.4	9.04×10^5	(6.3)
	6.7-hr. I		3820	193.4	8.13×10^5	5.7
10	86-sec. I	23.4	4.03×10^5	1.307	5.26×10^5	2.8
	85-min. Ba	14.7	2.97×10^4	41.4	11.77×10^5	(6.3)
	6.7-hr. I		5500	193.4	11.70×10^5	6.3
11	86-sec. I	41.1	7.55×10^5	2.604	19.6×10^5	3.0
	85-min. Ba	26.4	3.52×10^4	123.2	41.5×10^5	(6.3)
	6.7-hr. I		7120	581.4	45.5×10^5	6.9
12	86-sec. I	21.4	4.49×10^5	2.604	11.66×10^5	3.8
	85-min. Ba	38.4	1.63×10^4	123.2	19.2×10^5	(6.3)
	6.7-hr. I		3210	581.4	20.5×10^5	6.7
Average	86-sec. I					3.1
	6.7-hr. I					6.3

TABLE III. Data used in calculation of fission yield of 86-sec. I from Pu^{239} irradiated in a metallic medium.

Run	Isotope analyzed	Chemical yield (percent)	Activity corr. for decay and chem. yield (c/m)	Corr. for saturation	Corrected saturation activity (c/m)	Fission yield (percent)
13	86-sec. I	40.0	8.88×10^4	2.604	2.31×10^5	1.8
	85-min. Ba	29.6	5784	123.2	6.82×10^5	(6.3)
	6.7-hr. I		1298	581.4	8.30×10^5	6.3
14	86-sec. I	23.2	1.72×10^5	2.604	4.47×10^5	2.3
	85-min. Ba	32.8	8463	123.2	9.98×10^5	(6.3)
	6.7-hr. I		2010	581.4	12.8×10^5	6.7
15	86-sec. I	40.2	1.93×10^5	2.604	5.03×10^5	1.8
	85-min. Ba	34.5	1.204×10^4	123.2	14.2×10^5	(6.3)
	6.7-hr. I					
16	86-sec. I	42.2	1.72×10^5	2.604	4.48×10^5	1.6
	85-min. Ba	31.3	1.21×10^4	123.2	14.2×10^5	(6.3)
	6.7-hr. I					
Average	86-sec. I					1.9
	6.7-hr. I					6.5

presented in Tables II–IV. The chemical yields are not given for 6.7-hr. I because each decay point was corrected separately for chemical yield. In addition to the correction factors given there, an absorption correction of 1.04 and a parent correction of 0.918 were used for the 85-min. Ba. The 6.7-hr. I gross activity was multiplied by 1.1 to correct for both absorption and the presence of longer-lived iodine components.

Table V gives a summary of the results. The measured values of the fission yields of 6.7-hr. I are somewhat higher than the previously reported values but the agreement is within experimental error. Perhaps an insufficient correction was used for subtracting the 22-hr. I activity. It appears probable, however, that in this series of experiments complete exchange with the added carrier was achieved. The fission yields of 86-sec. I are higher than measured in the first experiments but still much lower than the total chain yields. The first chemical procedure used for isolating the iodine from the irradiated solutions did not achieve complete radiochemical exchange under the conditions of the necessary rapid operations. The reasons for the low precision in the second series of determinations are not entirely clear. The longer-lived components were subtracted from each decay curve and then a least squares analysis was applied to the remaining points. Since counting in these runs did not start until about 6 or 7 minutes after the end of irradiation most of the points for the resolved 86-sec. I decay curves were lower than the tails of the unresolved curves.

The observed fraction (fourth row of Table V) of the total chain yield (third row) which each 86-sec. I fission yield represents is considerably lower than that predicted by the postulate of equal chain length[12] (fifth row). This postulate states that, when fission occurs, the most probable charge distribution for each mass ratio is that which leads to equal chain lengths for the two fragments. The postulate is based on very meager evidence. If there were an independent isomer of the 86-sec. I, the observed fission yield of the latter would necessarily be low, as part of the chain would be along the isomer. If its half-life were 30 seconds or less it would not have been observed in these experiments. An alternative explanation is that the missing fraction of total chain yield is due to production of the Xe daughter as a primary fission fragment. The total Xe^{136} yield from U^{235} fission has been reported[13] as 2.23 times the yield of Xe^{131}. Taking 2.8 percent[14] for the yield of the latter, the fission yield of Xe^{136} is then 6.2 percent. Another reason for the low 86-sec. I fission yields might have been the existence of a Te parent whose half-life is greater than about 20 seconds. Therefore some experiments were performed to learn something about such a possible parent.

HALF-LIFE OF Te PARENT

Three semi-quantitive runs were made as follows: A uranyl nitrate solution was irradiated for two minutes and the iodine which was extracted 1.3 minutes later was discarded. Then another iodine extraction was made after 1.2 minutes more had elapsed. This was purified and counted through 513 mg Al/cm². The amount of 86-sec. I found was compared with the amount found in three earlier runs

[12] L. E. Glendenin, C. D. Coryell, and R. R. Edwards, Manhattan Project Report CL-LEG No. 1, July 25, 1946; see also R.D. Present, Phys. Rev. **72**, 7 (1947).

[13] H. G. Thode and R. L. Graham, Can. J. Research **25A**, 1 (1947).

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TABLE IV. Data used in calculation of fission yield of 86-sec. I from U^{233} irradiated in a metallic medium.

Run	Isotope analyzed	Chemical yield (percent)	Activity corr. for decay and chem. yield (c/m)	Corr. for saturation	Corrected saturation activity (c/m)	Fission yield (percent)
17	86-sec. I	35.6	7.19×10^{4}	2.604	1.87×10^{5}	1.5
	85-min. Ba	38.4	6.56×10^{3}	123.2	7.74×10^{5}	(6.3)
18	86-sec. I	25.1	9.50×10^{5}	2.604	2.47×10^{6}	1.7
	85-min. Ba	42.3	7.28×10^{3}	123.2	8.59×10^{5}	(6.3)
19	86-sec. I	24.1	1.46×10^{5}	2.604	3.80×10^{5}	2.1
	85-min. Ba	50.4	9.40×10^{3}	123.2	11.1×10^{5}	(6.3)
20	86-sec. I	37.3	1.08×10^{5}	2.604	2.81×10^{5}	1.3
	85-min. Ba	18.8	1.07×10^{4}	123.2	12.6×10^{5}	(6.3)
Average	86-sec. I					1.7

TABLE V. Summary of fission yield results.

	U^{235}	Pu^{239}	U^{233}
Fission yield of 86-sec. I	3.1 ±0.4 percent	1.9 ±0.3 percent	1.7 ±0.3 percent
Total chain yield	6.2	5.8	6.0
Observed fraction of chain yield	50	33	28
Predicted fraction of chain yield	87	77	57
Fission yield of 6.7-hr. I — Observed	6.3	6.5	
Fission yield of 6.7-hr. I — Values in literature	5.6	5.6	

where the conditions were the same except that the first iodine extracts were counted and the second extracts were not made. Any 86-sec. I found in the second extract can arise only from incomplete separation in the first one or from new 86-sec. I growing in from a Te parent. On the basis of the latter assumption, upper limits of 52-sec., 30-sec. and 20-sec., were set for the half-life of the Te. It is obvious that the last run gave the most complete separation for the first extraction. Since chemical yields were not measured in these runs, the activity in the second extraction was always multiplied by 2 in order to make certain that a low activity was not caused by a low chemical yield. In other similar runs where chemical yields were measured, they never varied by more than 30 percent. Data for the last run which are given in Table VI indicate that the 86-sec. I which was observed as a U fission product does not have a Te parent whose half-life is greater than 20 seconds.

Since a U^{235} fission yield of about 3.1 percent (6.2–3.1) for the chain of which 86-sec. I is a part, remained unaccounted for, a search was made for a longer lived Te parent. Some uranyl nitrate was irradiated for one hour, iodine was extracted 10.0 minutes thereafter and discarded; 2.2 minutes later iodine was extracted again and counted. No 86-sec. I was observed, but an amount which corresponds to 700 c/m at the time of the second extraction could easily have been detected. This was multiplied by 2 and compared with 130,000 c/m which was the average amount present at the end of a 2-minute bombardment as determined from the three runs mentioned above. From these data upper limits for the fission yield of the possible Te parent were calculated assuming various half-lives. These are listed in Table VII. It is seen that no appreciable amount of 86-sec. I could have remained undetected because of a Te parent. Furthermore, such a parent would almost certainly have been discovered earlier if its half-life were longer than a few hours.

In these iodine separations from the uranyl nitrate solutions the NaOCl method was relied upon to accomplish exchange. The conclusions are based on the assumption that most of the 86-sec. I which might have been formed from a Te parent would be separated from the solution at the second extraction. Any 86-sec. I coming out in the second separation because of incomplete extraction in the first iodine separation tends to compensate for any deviation from this assumption. Therefore the conclusions about the half-life of a possible Te parent are very probably correct.

MASS ASSIGNMENT

If the mass number of 86-sec. I were 137, its 3.4-min. Xe^{137} daughter would have been seen in the total iodine decay curve. Likewise, if the mass were 139, the 41-sec. Xe^{139} and the 7-min. Cs^{139} decay products would have shown up. From the Xe extraction experiments of Seelmann-Eggebert and Born[2] it appears that 17-min. Xe^{138} and 32-min. Cs^{138} are also not decay products of 86-sec. I. This observation was checked in the present work as follows. A quantity of uranyl nitrate solution was irradiated, iodine was extracted, and a small aliquot thereof was counted. The remainder of the iodine was allowed to decay for about 25 minutes and then Cs extracted. The amount of 32-min. Cs observed was compared with the amount which would have been observed had it grown in from an 86-sec. I grandparent. This was calculated from the activity of 86-sec. I which was counted. The first experiment gave a ratio for the calculated Cs to observed Cs of about 9. This was not sufficiently convincing evidence because of the small value of the ratio and the semi-quantitative nature of the experiment. A possible reason for the appearance of the 32-min. Cs^{138} could have been that some 17-min. Xe^{138} carried through with iodine in the chemical analysis. Therefore in the next experiment special precautions were taken to remove Xe. These consisted of boiling the iodide solution vigorously for 15 seconds immediately after its purification and then precipitation of PdI_2. This was dissolved 27 minutes later and analyzed for 32-min. Cs^{138}. None was detected.

TABLE VI. Data on half-life of possible Te parent.

Average activity of 86-sec. I from 3 previous runs at time of 1st extraction from U (1.3 min. after end of bombardment)	71,000 c/m
Activity of 86-sec. I in 2nd extraction corrected to time of separation from U and multiplied by 2	1200 c/m
Time from end of bombardment to 1st extraction in this run	1.40 min.
Time between the two extractions	1.23 min.
Upper limit on half-life of Te parent	20 sec.

TABLE VII. Upper limits on the fission yield of a possible Te parent.

Assumed $T_{\frac{1}{2}}$ of Te parent	2 min.	3 min.	5 min.	10 min.	20 min.	1 hr.
Max. possible fission yield (percent)	1.1	0.3	0.11	0.05	0.04	0.05
Assumed $T_{\frac{1}{2}}$ of Te parent	3 hr.	10 hr.	20 hr.	2 days	3 days	4 days
Max. possible fission yield (percent)	0.11	0.34	0.67	1.6	2.4	3.1

An activity which corresponds to 50 c/m at the time of Cs separation could have been detected. The 86-sec. I activity at the time when the PdI_2 was precipitated was found to be 1.0×10^7 c/m from counting an aliquot. This would have decayed after 27 minutes into 2×10^5 c/m of 32-min. Cs if its mass number were 138. The ratio of calculated to observed Cs is then 4000. One more run gave a ratio of 400; apparently the 17-min. Xe^{138} was not removed as effectively as in the previous run. However, it is well established from these experiments that 86-sec. I does not decay to 17-min. Xe^{138} and 32-min. Cs^{138}.

Since it seems very likely that the mass is below 137 an attempt was made to prove this by bombarding stable Xe with fast neutrons and analyzing it for 86-sec. I. The highest mass number for natural Xe is 136, and masses of 134 and 132 are present also. Active iodine might be produced from these by (n, p) reactions; if 86-sec. I were formed its mass could not be above 136. In three experiments 100 ml samples of Xe at 40 cm Hg pressure were irradiated in the center of the water boiler. Essentially no 86-sec. I was found, but this could have been due to the lack of a sufficiently high flux of neutrons with an energy above the threshold for the reaction.

Mass numbers 131, 133, and 135 are ruled out because 8-day I, 22-hr. I, and 6.7-hr. I, respectively are assigned to these. If 86-sec. I were isomeric with any of these, the total fission yield would be increased to a value considerably greater than that given by the mass-yield curve.[13] Masses 132 and 134 were recently assigned[4] to 2.4-hr. I and 54-min. I, respectively. From similar considerations of fission yield, 86-sec. I is probably not isomeric with these either. Mass numbers 133 and 134 are also improbable for another reason: 60-min Te^{133} and 43-min. Te^{134} cannot decay to 86-sec. I with a fission yield greater than 0.05 percent as shown in Table VII.

The possibility that 86-sec. I decays to a long-lived isomeric state of 3.4-min. Xe^{137} or of 17-min. Xe^{138} has not been ruled out. Nevertheless the most probable assignment of 86-sec. I is to mass 136.

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A General Method of Obtaining Molecular Symmetry Coordinates*

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A general method of obtaining molecular symmetry coordinates based on the algebra of group representation theory is described. The method is direct and involves no trial and error. It presupposes a knowledge of the irreducible representations of the molecular symmetry group rather than merely of their characters. The orthogonality properties of the symmetry coordinates are derived. As an example, the method is applied to boron trifluoride (D_{3h}), with the use of both internal and Cartesian coordinates.

INTRODUCTION

To factor the secular equation for the normal vibration frequencies of symmetrical molecules, so-called symmetry coordinates are usually employed. These are coordinates that form the basis for a completely reduced representation of the molecular symmetry group. Each symmetry coordinate belongs to one of the irreducible representations of this group, i.e., to one of the symmetry species into which the normal modes of vibration may be divided. There must be as many independent symmetry coordinates belonging to each irreducible representation as there are normal vibrations belonging to it.

Symmetry coordinates were introduced by Brester[1] who first showed how symmetry can be utilized to classify molecular vibrations. Wigner[2] treated this problem with the aid of group theory. Rosenthal,[3] Howard and Wilson,[4] Manneback,[5] Redlich and Tompa,[6] and others,[7] have developed methods of applying various kinds of symmetry coordinates to calculate normal vibration frequencies for symmetrical molecules.

At first the symmetry coordinates were formed as linear combinations of the $3n$ Cartesian coordinates that describe small displacements of the n atomic nuclei in the molecule. If $3n$ such symmetry coordinates are used, the complete secular equation will have six zero roots. These may be eliminated, and the secular equation reduced to the order $3n-6$, by the use of the momentum or Eckart conditions.[8] Recently, Wilson[9] has introduced symmetry coordinates constructed from $3n-6$ or more "internal" coordinates, such as changes in bond distances or bond angles. It can be proved that these symmetry coordinates satisfy the Eckart conditions.

Although several helpful rules have been given for obtaining various types of symmetry coordinates,[10] no perfectly general mathematical procedure has been given, and except for the simplest molecules, the finding of symmetry coordinates has involved a considerable amount of trial and error. It is the purpose of the present paper to describe a general group-theoretical method for obtaining molecular symmetry coordinates. For non-degenerate irreducible representations, the method is identical with that given by Eyring, Walter, and Kimball[11] for obtaining wave functions belonging to a given representation.

DETERMINATION OF SYMMETRY COORDINATES

The method is based on the algebra of group representation theory.[12] It will not be necessary to state the theorems used in their general form, but we shall derive them in a special and somewhat modified form that is convenient and sufficiently general for our purpose.

Let the molecular symmetry group have the order h, and let R denote any one of the symmetry operations.

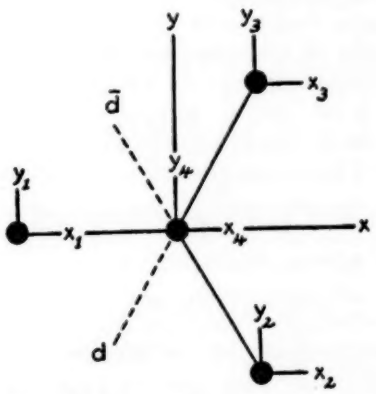

FIG. 1. Model (D_{3h}) of the boron trifluoride molecule and Cartesian coordinate system used.

* This work has been supported by Contract N7onr-398, Task Order I, with the ONR.

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TABLE I. Internal symmetry coordinates for BF_3 (D_{3h}).

Generating coordinate	Normalized symmetry coordinate
δ_1	$S(A_1') = 1/\sqrt{3}(\delta_1+\delta_2+\delta_3)$
γ	$S(A_2'') = \gamma$
δ_1	$S_{11}(E') = 1/(6)^{\frac{1}{2}}(2\delta_1-\delta_2-\delta_3)$
—	$S_{12}(E') = 1/\sqrt{2}(\delta_2-\delta_3)$
α_{12}	$S_{21}(E') = 1/(6)^{\frac{1}{2}}(\alpha_{12}+\alpha_{23}-2\alpha_{31})$
—	$S_{22}(E') = 1/\sqrt{2}(\alpha_{23}-\alpha_{12})$

Let D^j be an irreducible representation of dimension l_j. If the symmetry coordinates $\mathcal{S}^j{}_{k1}$, $\mathcal{S}^j{}_{k2}$, $\cdots$, $\mathcal{S}^j{}_{kl_j}$ transform according to the rule

$$R\mathcal{S}^j{}_{k\alpha} = \sum_{\beta=1}^{l_j} \mathcal{S}^j{}_{k\beta} D^j(R)_{\beta\alpha}, \tag{1}$$

they are said to belong to the irreducible representation D^j. The subscript k is used to differentiate this subset of symmetry coordinates from others belonging to the same irreducible representation. The symmetry coordinate $\mathcal{S}^j{}_{k\alpha}$ is said to belong to the α'th row of the irreducible representation D^j. This latter statement is meaningful only when the irreducible representation is completely given, rather than determined except for an arbitrary similarity transformation. In what follows we shall assume all of the irreducible representations of the molecular symmetry group to be completely determined. For convenience, we shall further assume that they have been chosen in such a manner that all of their matrices are real orthogonal.

The matrix elements of two irreducible representations D^j and $D^{j'}$ of the molecular symmetry group satisfy the fundamental relation

$$\sum_R D^j(R)_{\alpha\beta} D^{j'}(R)_{\alpha'\beta'} = (h/l_j)\delta_{jj'}\delta_{\alpha\alpha'}\delta_{\beta\beta'}, \tag{2}$$

where the sum is extended over all members of the group, i.e., over all symmetry operations, and where the Kronecker δ-symbol (e.g., $\delta_{jj'}=1$ when $j=j'$, $\delta_{jj'}=0$ when $j\neq j'$) is used on the right.

If we multiply Eq. (1) by $D^{j'}(R)_{\beta'\alpha'}$, sum over all members R of the group, and apply Eq. (2), the result is

$$\sum_R D^{j'}(R)_{\beta'\alpha'} R\mathcal{S}^j{}_{k\alpha} = (h/l_j)\delta_{jj'}\delta_{\alpha\alpha'}\mathcal{S}^j{}_{k\beta'}. \tag{3}$$

For $j'=j$, $\alpha'=\beta'=\alpha$, this reduces to

$$\sum_R D^j(R)_{\alpha\alpha} R\mathcal{S}^j{}_{k\alpha} = (h/l_j)\mathcal{S}^j{}_{k\alpha}. \tag{4}$$

On the other hand, for $j'=j$, $\alpha'=\alpha$, and $\beta'=\beta$, Eq. (3) becomes

$$\sum_R D^j(R)_{\beta\alpha} R\mathcal{S}^j{}_{k\alpha} = (h/l_j)\mathcal{S}^j{}_{k\beta}. \tag{5}$$

Thus, Eqs. (4) and (5) are necessary conditions that the quantities $\mathcal{S}^j{}_{k1}$, $\mathcal{S}^j{}_{k2}$, $\cdots$, $\mathcal{S}^j{}_{kl_j}$ belong to the irreducible representation D^j, or more particularly, that they transform under group operations according to Eq. (1). In Appendix I it is shown that Eq. (4) is also the sufficient condition that $\mathcal{S}^j{}_{k\alpha}$ and its "partners" determined by Eq. (5) transform according to Eq. (1). Thus, if a single symmetry coordinate $\mathcal{S}^j{}_{k\alpha}$ satisfying Eq. (4) can be found, this coordinate, together with its l_j-1 partners defined explicitly by Eq. (5), will form a subset of symmetry coordinates belonging to the irreducible representation D^j.

We shall now give a simple procedure for obtaining a symmetry coordinate satisfying Eq. (4). Let the (Cartesian, internal, or other) coordinates used to describe an arbitrary small distortion or displacement of the semi-rigid molecule be denoted by r_i. Any linear combination $L(r_i)$ of these coordinates can also be written as a linear function of a complete set of symmetry coordinates, i.e.,

$$L = \sum_{j'} \sum_k \sum_\beta C^{j'}{}_{k\beta} \mathcal{S}^{j'}{}_{k\beta}, \tag{6}$$

where the $C^{j'}{}_{k\beta}$ are constants.

Now, if we operate on L with any member R of the molecular symmetry group, multiply by $D^j(R)_{\alpha\alpha}$, sum over all members of the group, and apply Eqs. (1) and (2), we obtain:

$$\begin{aligned}\sum_R D^j(R)_{\alpha\alpha} RL &= \sum_{j'} \sum_k \sum_\beta \sum_R C^{j'}{}_{k\beta} D^j(R)_{\alpha\alpha} R\mathcal{S}^{j'}{}_{k\beta} \\ &= \sum_{j'} \sum_k \sum_\beta C^{j'}{}_{k\beta}(h/l_j)\delta_{jj'}\delta_{\alpha\beta}\mathcal{S}^{j'}{}_{k\alpha} \\ &= (h/l_j) \sum_k C^j{}_{k\alpha}\mathcal{S}^j{}_{k\alpha}. \end{aligned} \tag{7}$$

Since $\sum C^j{}_{k\alpha}\mathcal{S}^j{}_{k\alpha}$ is a linear combination of symmetry coordinates that satisfy Eq. (4), it will itself satisfy Eq. (4), and so will the left member of Eq. (7).

These results provide the following method for obtaining symmetry coordinates. Choose a linear function L_k of the coordinates r_i. Then the sum

$$S^j{}_{k\alpha} = (l_j/h) \sum_R D^j(R)_{\alpha\alpha} RL_k \tag{8}$$

will be a symmetry coordinate belonging to the α'th row of the irreducible representation D^j, and its l_j-1 partners will be given by

$$S^j{}_{k\beta} = (l_j/h) \sum_R D^j(R)_{\beta\alpha} RS^j{}_{k\alpha}. \tag{9}$$

As indicated by the subscript k, there are often more than one subset of symmetry coordinates belonging to a given irreducible representation. If a_j subsets of symmetry coordinates belong to the irreducible representation D^j, it will be necessary to choose a_j linear combinations $L_k(r_i)$ such that application of Eq. (8) to each of them yields a_j symmetry coordinates $S^j{}_{k\alpha}(k=1, 2, \cdots, a_j)$ that are linearly independent in terms of the r_i. The partners of each of these are then obtained by Eq. (9).

That it is possible in this manner to obtain the requisite number of independent[13] sets of symmetry co-

[13] The term "independent" as applied to symmetry coordinates is ambiguous. It may mean linearly independent in terms of all of the coordinates r_i, irrespective of whether or not their number exceeds the degrees of freedom of the molecular motions they are intended to describe; it may denote linear independence in terms of $3n$ coordinates required to describe any arbitrary motion of the atoms in a molecule; or it may mean linear independence in terms of a set of $3n-6$ coordinates describing an arbitrary distortion of a (non-linear) semi-rigid molecule. Wherever not explicitly stated in the present paper, the meaning should be clear from the context.

ordinates belonging to each irreducible representation is proved in Appendix II. In fact, it is shown there that it is sufficient to put each of the linear functions $L_k(\mathbf{r}_i)$ appearing in Eq. (8) equal to a single one of the coordinates $\mathbf{r}_i$.

ORTHOGONALITY PROPERTIES OF SYMMETRY COORDINATES

Let two symmetry coordinates, expressed in terms of the coordinates $\mathbf{r}_i$, be

$$S^i{}_{k\alpha}=\sum_i u^i{}_{k\alpha,i}\mathbf{r}_i \quad \text{and} \quad S^{i'}{}_{k'\alpha'}=\sum_i u^{i'}{}_{k'\alpha',i}\mathbf{r}_i.$$

The scalar product of these symmetry coordinates in the space of the $\mathbf{r}_i$ is defined as

$$(S^i{}_{k\alpha}\cdot S^{i'}{}_{k'\alpha'})=\sum_i u^i{}_{k\alpha,i}u^{i'}{}_{k'\alpha',i}.$$

If this quantity vanishes, the symmetry coordinates are said to be orthogonal in the space of the original coordinates $\mathbf{r}_i$. If $(S^i{}_{k\alpha}\cdot S^i{}_{k\alpha})=1$, $S^i{}_{k\alpha}$ is said to be normalized to unity.

Any two symmetry coordinates belonging to different irreducible representations or to different rows of the same irreducible representation are orthogonal in the $\mathbf{r}_i$-space. To prove this, we first observe that

$$(S^i{}_{k\alpha}\cdot S^{i'}{}_{k'\alpha'})=(RS^i{}_{k\alpha}\cdot RS^{i'}{}_{k'\alpha'}), \tag{10}$$

since the operation R is orthogonal. Applying Eq. (1) to Eq. (10), we get

$$\begin{aligned}(S^i{}_{k\alpha}\cdot S^{i'}{}_{k'\alpha'})&=(\textstyle\sum_\beta S^i{}_{k\beta}D^i(R)_{\beta\alpha}\cdot\sum_{\beta'} S^{i'}{}_{k'\beta'}D^{i'}(R)_{\beta'\alpha'})\\&=\textstyle\sum_\beta\sum_{\beta'} D^i(R)_{\beta\alpha}D^{i'}(R)_{\beta'\alpha'}(S^i{}_{k\beta}\cdot S^{i'}{}_{k'\beta'}).\end{aligned}$$

Summation of this over all members of the group and application of Eq. (2) give

$$\begin{aligned}h(S^i{}_{k\alpha}\cdot S^{i'}{}_{k'\alpha'})&=\textstyle\sum_\beta\sum_{\beta'}(h/l_j)\delta_{jj'}\delta_{\alpha\alpha'}\delta_{\beta\beta'}(S^i{}_{k\beta}\cdot S^{i'}{}_{k'\beta'})\\&=(h/l_j)\delta_{jj'}\delta_{\alpha\alpha'}\textstyle\sum_\beta(S^i{}_{k\beta}\cdot S^{i'}{}_{k'\beta}),\end{aligned} \tag{11}$$

from which the theorem follows.

On the other hand, two symmetry coordinates belonging to the same row of a given irreducible representation, but to different subsets, will not always be orthogonal when determined by the method described in the preceding section. However, it is not difficult to make them orthogonal, and this will usually be a convenience. Let $S^i{}_{k\alpha}$ and $S^i{}_{k'\alpha}$ be two such coordinates. According to Eq. (11)

$$(S^i{}_{k\alpha}\cdot S^i{}_{k'\alpha})=(1/l_j)\sum_{\beta=1}^{l_j}(S^i{}_{k\beta}\cdot S^i{}_{k'\beta}).$$

The right member is independent of α; hence

$$(S^i{}_{k1}\cdot S^i{}_{k'1})=(S^i{}_{k2}\cdot S^i{}_{k'2})=\cdots=(S^i{}_{kl_j}\cdot S^i{}_{k'l_j}). \tag{12}$$

Thus, if one of these scalar products vanishes, all of them will vanish.

The following procedure was therefore adopted. Whenever the symmetry coordinates belonging to the first row of a given irreducible representation, as obtained by means of Eq. (8), are not all mutually orthogonal, mutually orthogonal linear combinations of them are formed by Schmidt's orthogonalization procedure.[14] These linear combinations, which are also symmetry coordinates belonging to the first row of the irreducible representation in question, are then used instead of the original symmetry coordinates, and their partners are determined by Eq. (9).

TABLE II. Set of $3n$ orthonormal symmetry coordinates for boron trifluoride (D_{3h}).

Generating coordinate	Normalized symmetry coordinate
x_1	$S(A_1')=12^{-\frac{1}{2}}(2x_1-x_2+\sqrt{3}y_2-x_3-\sqrt{3}y_3)$
y_1	$S(A_2')=12^{-\frac{1}{2}}(2y_1-\sqrt{3}x_2-y_2+\sqrt{3}x_3-y_3)$
z_1	$S_1(A_2'')=3^{-\frac{1}{2}}(z_1+z_2+z_3)$
z_4	$S_2(A_2'')=z_4$
x_1	$S_{11}(E')=24^{-\frac{1}{2}}(4x_1+x_2-\sqrt{3}y_2+x_3+\sqrt{3}y_3)$
—	$S_{12}(E')=24^{-\frac{1}{2}}(-\sqrt{3}x_2+3y_2+\sqrt{3}x_3+3y_3)$
(x_2)	$S_{21}(E')=24^{-\frac{1}{2}}(3x_2+\sqrt{3}y_2+3x_3-\sqrt{3}y_3)$
—	$S_{22}(E')=24^{-\frac{1}{2}}(4y_1+\sqrt{3}x_2+y_2-\sqrt{3}x_3+y_3)$
x_4	$S_{31}(E')=x_4$
—	$S_{32}(E')=y_4$
z_2	$S_{11}(E'')=2^{-\frac{1}{2}}(z_2-z_3)$
—	$S_{12}(E'')=6^{-\frac{1}{2}}(-2z_1+z_2+z_3)$

EXAMPLE: BORON TRIFLUORIDE (D_{3h})

This example has been chosen for its simplicity. A more complex example would bring out better the power of the method. We shall first use internal coordinates chosen as follows: δ_1, δ_2, δ_3 denote infinitesimal increments in the three BF distances, α_{12}, α_{23}, α_{31} denote small changes in the three F–B–F angles, and γ denotes a small out-of-plane displacement of the boron atom. Of the $3n-6=6$ normal vibrations, one belongs to each of the irreducible representations A_1' and A_2'', and two sets of doubly degenerate vibrations belong to the two-dimensional representation E'. The characters for the one-dimensional irreducible representations of D_{3h}[15] are identical with the matrices of these representations. The matrices for the representation E' were chosen as the transformation matrices for translations T_x, T_y in the plane of the molecule.

Using as "generating coordinates" to be substituted in Eq. (8) the internal coordinates listed in the first column of Table I, we obtain from Eqs. (8) and (9) the symmetry coordinates listed in the second column. Since $S_{11}(E')$ and $S_{21}(E')$ are orthogonal, there is no need for any orthogonalization procedure. When α_{12} is used as "generating coordinate," a symmetry coordinate $\alpha_{12}+\alpha_{23}+\alpha_{31}$ belonging to A_1' is obtained. However, this vanishes, since the sum of the three F–B–F angles is 360°. Thus, the redundancy in the choice of internal coordinates has been taken into account, and Table I

[14] See for example, H. Margenau and G. M. Murphy, *The Mathematics of Physics and Chemistry* (D. Van Nostrand Company, Inc., New York, 1943), p. 298; or G. Birkhoff and S. MacLane, *A Survey of Modern Algebra* (The Macmillan Company, New York, 1941), p. 187.

[15] Character tables may be found in reference 7 or in G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules*, (D. Van Nostrand Company, Inc., New York, 1945).

TABLE III. Set of $3n-6$ orthonormal symmetry coordinates for boron trifluoride (D_{3h}) orthogonal to translations and rotations

$$\begin{aligned}
\bar{S}(A_1') &= 12^{-\frac{1}{2}}(2x_1-x_2+\sqrt{3}y_2-x_3-\sqrt{3}y_3)\\
\bar{S}(A_2'') &= (3m^2+M^2)^{-\frac{1}{2}}[M(z_1+z_2+z_3)-3mz_4]\\
\bar{S}_{11}(E') &= (9m^2+3M^2)^{-\frac{1}{2}}[M(x_1+x_2+x_3)-3mx_4]\\
\bar{S}_{12}(E') &= (9m^2+3M^2)^{-\frac{1}{2}}[M(y_1+y_2+y_3)-3my_4]\\
\bar{S}_{21}(E') &= 12^{-\frac{1}{2}}(2x_1-x_2-\sqrt{3}y_2-x_3+\sqrt{3}y_3)\\
\bar{S}_{22}(E') &= 12^{-\frac{1}{2}}(-2y_1-\sqrt{3}x_2+y_2+\sqrt{3}x_3+y_3)
\end{aligned}$$

includes the proper number of independent symmetry coordinates.

We shall now solve the same problem using the Cartesian coordinates defined in Fig. 1. x_i, y_i, z_i are the components of the infinitesimal displacement of the i'th atom from its equilibrium position. Application of the general procedure yields the set of twelve symmetry coordinates listed in Table II. The "generating coordinates" used are given in the first column. In the case of $S_{21}(E')$, the generating coordinate is put in parenthesis; for when this coordinate is used, an expression is obtained for $S_{21}(E')$ which is not orthogonal to $S_{11}(E')$. Orthogonalization by Schmidt's method gives the expression for $S_{21}(E')$ listed in the table.

The Eckart conditions lead to the following relations between the symmetry coordinates

$$\begin{aligned}
S(A_2') &= 0,\\
\sqrt{3}mS_1(A_2'')+MS_2(A_2'') &= 0,\\
(3/2)^{\frac{1}{2}}m[S_{11}(E')+S_{21}(E')]+MS_{31}(E') &= 0,\\
(3/2)^{\frac{1}{2}}m[S_{12}(E')+S_{22}(E')]+MS_{32}(E') &= 0,\\
S_{11}(E'') &= 0,\\
S_{12}(E'') &= 0,
\end{aligned} \qquad (13)$$

Here M is the mass of the boron atom and m, the mass of a fluorine atom. By means of these equations it is easy to eliminate six symmetry coordinates from the potential and kinetic energy functions.

If it is desired to choose T_x, T_y, $\cdots$, R_z as members of a new set of orthogonal symmetry coordinates, this can be done as follows. The rotations are already present among the symmetry coordinates listed in Table II. In fact, $R_x=S_{11}(E'')$, $R_y=-S_{12}(E'')$, and $R_z=S(A_2')$. The translation T_z belongs to A_2''. If $S_1(A_2'')$ and $S_2(A_2'')$ are subjected to a transformation defined by the matrix

$$\begin{pmatrix} \sqrt{3}\mu m & \mu M \\ \mu M & -\sqrt{3}\mu m \end{pmatrix}, \quad \text{where} \quad \mu=(3m^2+M^2)^{-\frac{1}{2}},$$

one of the new symmetry coordinates will be T_z. Since this matrix is orthogonal, the other symmetry coordinate will be orthogonal to T_z and will be normalized.

The translations T_x and T_y belong to E'. If $S_{11}(E')$, $S_{21}(E')$, and $S_{31}(E')$, and also $S_{12}(E')$, $S_{22}(E')$, and $S_{32}(E')$, are transformed by the matrix

$$\begin{bmatrix} (3/2)^{\frac{1}{2}}\mu m & (3/2)^{\frac{1}{2}}\mu m & \mu M \\ -(1/2)^{\frac{1}{2}}\mu M & -(1/2)^{\frac{1}{2}}\mu M & \sqrt{3}\mu m \\ (1/2)^{\frac{1}{2}} & -(1/2)^{\frac{1}{2}} & 0 \end{bmatrix}$$

T_x and T_y will appear as the first coordinate of each set. This is assured by the choice of the first row of the matrix. The other rows are chosen so as to make the matrix orthogonal, thereby assuring that the other four symmetry coordinates form two orthonormal subsets orthogonal to T_x and T_y.

The six symmetry coordinates obtained in this manner are listed in Table III. Together with the translations and rotations they form a complete orthonormal set. They are equivalent to the symmetry coordinates obtained by Silver and Schaffer from mass-reduced Cartesian coordinates.[16]

APPENDIX I

By means of well-known theorems of group theory[17] we find

$$\begin{aligned}
\Sigma_P D^i(P)_{\alpha\gamma}PS^i{}_{k\gamma} &= \Sigma_P D^i(R^{-1}P)_{\alpha\gamma}R^{-1}PS^i{}_{k\gamma}\\
&= \Sigma_P \Sigma_\beta D^i(R^{-1})_{\alpha\beta}D^i(P)_{\beta\gamma}R^{-1}PS^i{}_{k\gamma}\\
&= R^{-1}\Sigma_\beta D^i(R)_{\beta\alpha}\Sigma_P D^i(P)_{\beta\gamma}PS^i{}_{k\gamma},
\end{aligned}$$

whence

$$R\Sigma_P D^i(P)_{\alpha\gamma}PS^i{}_{k\gamma} = \Sigma_\beta D^i(R)_{\beta\alpha}\Sigma_P D^i(P)_{\beta\gamma}PS^i{}_{k\gamma}.$$

Application of Eqs. (4) and (5) to this equation gives

$$RS^i{}_{k\alpha} = \Sigma_\beta S^i{}_{k\beta}D^i(R)_{\beta\alpha},$$

which is Eq. (1). Thus a function $S^i{}_{k\alpha}$ satisfying Eq. (4), together with its partners determined by Eq. (5), will transform according to Eq. (1).

APPENDIX II

A complete set of independent symmetry coordinates is known to exist. If a_j subsets of symmetry coordinates belong to the irreducible representation D^j, we have a_j equations of the form

$$S^i{}_{k\alpha} = (l_j/h)\,\Sigma_R D^i(R)_{\alpha\alpha}RS^i{}_{k\alpha}. \qquad (14)$$

The symmetry coordinates can be expressed in terms of the internal coordinates r_i as follows

$$S^i{}_{k\alpha} = \Sigma_i b^i{}_{ki}r_i,$$

where the $b^i{}_{ki}$ are constants. If this is substituted into Eq. (14) the following set of a_j equations are obtained.

$$\begin{aligned}
\Sigma_i b^i{}_{1i}\{(l_j/h)\,\Sigma_R D^i(R)_{\alpha\alpha}Rr_i\} &= S^i{}_{1\alpha}\\
\Sigma_i b^i{}_{2i}\{(l_j/h)\,\Sigma_R D^i(R)_{\alpha\alpha}Rr_i\} &= S^i{}_{2\alpha}\\
\cdots\cdots\cdots

Letters to the Editor

THIS section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section should not exceed 600 words in length and must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

The Energy Difference between the Rotational Isomers of 1,2-Dichloroethane

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May 12, 1949

UNDER the same title Bernstein[1] has recently published a paper, in which he has determined the energy difference between the rotational isomers of 1,2-dichloroethane as $\Delta E = 1100 \pm 50$ cal/mole from the variation of intensities of infra-red absorption bands with temperature. The same experiment was already carried out by us[2] in 1945 with the same result ($\Delta E = 1030$ cal/mole). In addition to this infra-red experiment we measured the variation of the apparent dipole moment with temperature, from which we found $\Delta E = 1210$ cal/mole.[3] The result of our electron diffraction experiment[4] for gaseous 1,2-dichloroethane could also be explained satisfactorily from this value of energy difference.

It will not be out of place to report the energy difference between the rotational isomers of 1,2-dibromoethane. From the variation of the intensities of absorption frequencies 1192 cm^{-1} (assigned to the *trans*-isomer) and 1236 cm^{-1} (assigned to the gauche isomer) with temperature we found $\Delta E = 1450$ cal/mole[2] and from the variation of apparent dipole moment with temperature $\Delta E = 1400$ cal/mole.[3]

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[2] Simanouti, Tsuruta, and Mizushima, Sci. Pap. Inst. Phys. Chem. Res., Tokyo, **42**, Chem. 51 (1945), see also Mizushima, Morino, Watanabe, Simanouti, and Yamaguchi, J. Chem. Phys. (accepted for publication).
[3] Watanabe, Mizushima, and Morino, J. Chem. Phys. **39**, 401 (1942).
[4] Yamaguchi, Morino, Watanabe, and Mizushima, J. Chem. Phys. **40**, 417 (1943).

Note on the Product Rule for Rotational Isomers

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May 12, 1949

QUITE recently Bernstein[1] has proposed the product rule for the rotational isomers of 1,2-dichloroethane and 1,2-dibromoethane and concluded that the less stable isomer cannot be of the *cis*-form, but he did not apply this rule to the gauche form. This product rule was already presented by us in 1942[2,3] and was applied to the *trans*- and gauche isomers of various dihalogenoethanes where the *trans*-form is the molecular configuration in which the two halogen atoms are at the farthest distance apart and the gauche form can be obtained from the *trans*-form through an internal rotation about the C—C axis by about 120°. In our case the application of this rule to the gauche form was possible, since we calculated the *G*-matrix for the general form with C_2 symmetry.[2]

For the vibrations symmetric to the C_2 axis of 1,2-dichloroethane we have

$$\frac{\pi\nu(trans\text{-})}{\pi\nu(\text{gauche})} = \frac{1052\times754\times300}{1031\times654\times265} = 1.33,$$

$$\left(\frac{|\mathbf{G}(trans\text{-})|}{|\mathbf{G}(\text{gauche})|}\right)^{\frac{1}{2}} = 1.24,$$

and for the vibrations antisymmetric to the same axis

$$\frac{\pi\nu(trans\text{-})}{\pi\nu(\text{gauche})} = \frac{709\times223}{677\times411} = \frac{1}{1.76'}$$

$$\left(\frac{|\mathbf{G}(trans\text{-})|}{|\mathbf{G}(\text{gauche})|}\right)^{\frac{1}{2}} = \frac{1}{1.81'},$$

where $\mathbf{G}$ is the *G*-matrix used in the normal vibration calculation due to Wilson.[4] The agreement between the theoretical and experimental values can be considered to be satisfactory, since we neglected in our calculation the hydrogen vibrations, the rotational oscillation about the C—C axis and the interaction between the two chlorine atoms.

Similarly for 1,2-chlorobromoethane we have

$$\frac{\pi\nu(trans\text{-})}{\pi\nu(\text{gauche})} = \frac{210\times251\times630\times726\times1052}{251\times385\times568\times665\times1023} = \frac{1}{1.44'}$$

$$\left(\frac{|\mathbf{G}(trans\text{-})|}{|\mathbf{G}(\text{gauche})|}\right)^{\frac{1}{2}} = \frac{1}{1.63'},$$

and for 1,2-chloroiodoethane we have

$$\frac{\pi\nu(trans\text{-})}{\pi\nu(\text{gauche})} = \frac{186\times232\times576\times707\times1046}{232\times368\times511\times660\times1107} = \frac{1}{1.74'}$$

$$\left(\frac{|\mathbf{G}(trans\text{-})|}{|\mathbf{G}(\text{gauche})|}\right)^{\frac{1}{2}} = \frac{1}{1.75}.$$

For the vibrations antisymmetric to the C_2 axis of 1,2-dibromoethane we have

$$\frac{\pi\nu(trans\text{-})}{\pi\nu(\text{gauche})} = \frac{1053\times660\times190}{1019\times551\times231} = 1.02,$$

$$\left(\frac{|\mathbf{G}(trans\text{-})|}{|\mathbf{G}(\text{gauche})|}\right)^{\frac{1}{2}} = 1.00,$$

but for the vibrations symmetric to this axis one of the frequencies was left undetermined. The value x of this frequency can be determined by use of the product rule:

$$\frac{\pi\nu(trans\text{-})}{\pi\nu(\text{gauche})} = \frac{651\times x}{583\times355'}$$

$$\left(\frac{|\mathbf{G}(trans\text{-})|}{|\mathbf{G}(\text{gauche})|}\right)^{\frac{1}{2}} = \frac{1}{1.94'},$$

$$x = 164 \text{ cm}^{-1}.$$

The determination of this frequency was especially important in our calculation of statistical entropy of 1,2-dibromoethane.[5]

Our experiment on the Raman effect,[6] dipole moment[7] and electron diffraction[8] could establish that the rotational isomers of 1,2-dihalogenoethanes are of the *trans*- and the gauche forms. This conclusion can thus be reconciled with the product rule as stated above.

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The Scattering of Light by Sodium Silicate Solutions*

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USING a 90° turbidimeter built in this laboratory the scattering of light by sodium silicate solutions has been investigated. This method was applied in order to determine if and when structures—presumably combining Si, O, and H atoms—larger than ordinary ions are present in such solutions.

In the case of sodium metasilicate (Na_2SiO_3), prepared by fusion of a pure quartz with C.P. sodium hydroxide and crystallization of a hydrate from a solution of the melt, it is possible to obtain reproducible results from solutions filtered through a carefully cleaned sintered stainless steel filter. The solutions were prepared from freshly recrystallized undried $Na_2SiO_3 \cdot 9H_2O$ crystals by dissolving them in freshly redistilled water; they were stored under an atmosphere of nitrogen.

These filtered metasilicate solutions give results, some of which are shown in Fig. 1. Below a concentration of 0.10 g/cc these results have been reproduced using three other groups of solutions in the same concentration range; the data at concentrations greater than 0.10 g/cc are the result of only one series of measurements. It is observed that the solutions have very small turbidities even at very high concentrations. Representing the data by a straight line, we can relate the turbidity, τ, to a weight average molecular weight, M, by the equation[1]

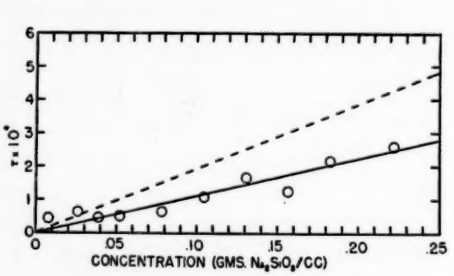

FIG. 1. Turbidity *versus* concentration for sodium metasilicate solutions. ——Least squares line from all data.– – –Calculated line for undissociated Na_2SiO_3 molecules.

$$\tau = HMc, \tag{1}$$

in which H is a refraction constant defined by the expression

$$H = \frac{32}{3}\pi^3 \frac{\mu_0^2}{N\lambda^4}\left(\frac{\mu-\mu_0}{c}\right)^2, \tag{2}$$

in which c is the concentration in g/cc, $\mu-\mu_0$ is the difference in index of refraction between the solution and the solvent, and λ is the wave-length in vacuum of the light used for the measurements. Using a τ/c value, namely 1.11×10^{-3} with a standard deviation in τ of $\pm0.21\times10^{-4}$, obtained from a least squares straight line, shown in Fig. 1, through all the available data and using $H=1.58\times10^{-5}$, calculated from $\mu-\mu_0$ measurements a molecular weight of 70.5 is calculated. If undissociated Na_2SiO_3 molecules ($M=122$) were present in the solutions, the $\tau-c$ relationship would be represented by the dotted line of Fig. 1 which corresponds to $\tau/c=1.93\times10^{-3}$. It is indicated by the fact that the experimental points lie below the dotted line that there is not only no aggregation in these metasilicate solutions, but that there is dissociation.

However, the above calculation of the molecular weight 70.5 assumes one type of molecule with one H value considered to be sufficient for representing the scattering. In a solution of dissociated ions each ionic specie will have its own H value and corresponding contribution to τ. The data should therefore be treated differently. We will assume that the solutions contain Na^+ ions and negatively charged complexes of Si, O, and perhaps H atoms. Measurements have been made of the refraction of silicate solutions with different SiO_2/Na_2O ratios. In one type the ratio was 1:1, in another 3.3:1. Assuming that the difference in index of refraction between solution and solvent is a linear function of the composition, as indicated by the ratio, it follows from the $\mu-\mu_0$ measurements that the polarizability of the Na^+ ion, α_1, is to the polarizability, α_2, per Si atom of the silicon complex as 20.5×10^{-24} cc is to 8.1×10^{-24} cc. These values are obtained by solving the following equations simultaneously

$$(\text{for } Na_2SiO_3)\ \mu-\mu_0 = n_1\alpha_1 + n_2\alpha_2 = n(\tfrac{2}{3}\alpha_1 + \tfrac{1}{3}\alpha_2)$$

$$(\text{for } Na_2O\ 3.3\ SiO_2)\ \mu-\mu_0 = n_1\alpha_1 + n_2\alpha_2 = n\left(\frac{2}{5.3}\alpha_1 + \frac{3.3}{5.3}\alpha_2\right),$$

since $\mu-\mu_0=n\alpha$. (n = number of molecules/cc.)

Considering now the case of the metasilicate alone, it follows that instead of our old value of H a new value should be used; this value is obtained from the old H by multiplying it by the correction factor

$$\frac{2\alpha_1^2+\alpha_2^2}{(2\alpha_1+\alpha_2)^2},$$

provided that total dissociation is assumed and that each silicon complex contains only one Si atom. The correction factor is 0.376, so in this case we would expect $\tau/c=0.73\times10^{-3}$ instead of the observed value $\tau/c=1.11\times10^{-3}$. At this point it seems futile to speculate about the reality of differences between the observed value and that calculated on the assumption of complete dissociation.

The metasilicate solutions had been standing a week or more before turbidity measurements were made. Some of the measurements were repeated several days to a week after the first measurement with little change in results. We therefore as yet have no evidence that complexes develop in these solutions in the course of time.

The importance of proper preparation and cleaning must be stressed. Unreproducible molecular weights of 800 to 1800 are found in metasilicate solutions prepared from dried crystals or commercial samples.

Preliminary investigations indicate that the solutions of the 3.3/1 SiO_2/Na_2O ratio sodium silicate have aggregates of a molecular weight $M=1500$ containing about twenty silicon atoms.

McCartney's[1] and Halwer's[2] work on sucrose solutions show that it is feasible to determine low molecular weights by light scattering. Our experiments seem to indicate that the method also can be used in order to obtain information about ionic dissociation.

* This work was supported by the Sodium Silicate Manufacturers Institute.
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Solutions of Salts Fluid at the Temperature of Liquid Nitrogen Spectra of Solutions of Rare Earths

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THE solutions were prepared in two steps. First, the salt was dissolved under more or less normal conditions rather than at low temperatures so that the rate of solution of the solid would not be excessively slow. The second step was one of dilution, a more rapid process, achieved by lowering the temperature of the original solution and then bubbling and condensing in from the gaseous state, solvent substances having low melting points.

In our experiments thus far, either *n*-propyl alcohol, *n*-butyl alcohol or *n*-propyl ether served as solvent for the first step and for the second, pairs of the following hydrocarbons in various proportions—methane, propane, propene, butene-1, and isopentane. A number of combinations proved to be homogeneous and fluid at the temperature of liquid nitrogen.

One of the above combined solvents was tested and found to remain fluid at about five degrees below the freezing point of nitrogen. Its composition was 1 part by volume of *n*-propyl alcohol, 4.5-parts liquid propane, and 4.5-parts liquid propene.

A number of hexahydrated rare earth bromides and nitrates were dissolved in such solvents, and absorption spectra were taken at the temperatures of liquid nitrogen. Solubilities of some of the rare earths were sufficient at 77°K for obtaining spectra in a path length of 25 cm. At a given concentration of a rare earth, (neodymium nitrate hexahydrate) the solution kept at 77°K for nine days remained clear and continued to give the same spectrum. When somewhat more was dissolved at about 175°K, a reduction in temperature to 77°K brought a quick appearance of turbidity, indicating that transformations were occurring at the low temperatures. The spectra of some of the dissolved salts became comparable in sharpness with those from their crystals at the low temperature. Bands arising at higher temperatures became resolved into lines at 77°K.

The line widths in the spectra of neodymium and samarium salts ranged from about one to five angstroms. The dissolved praseodymium and thulium salts gave more diffuse lines. The bromide and nitrate of neodymium showed strikingly different structures within corresponding groups, both in the spacings and numbers of component lines, indicating different symmetries of the fields about the positive ions. There were marked changes in the spectra on reducing the temperature from that of dry ice to that of liquid nitrogen. The refinement in the spectrum of samarium bromide hexahydrate was especially great on lowering the temperature.

Electrical conductances were measured over a range of temperatures and were found to drop rapidly at the lowest temperature, finally reaching in one solution 2×10^{-11} mhos for the specific conductance at 77°K.

Detailed descriptions of methods and results will be given in full detail in future papers.

We wish to express our indebtedness to Dr. Fred J. Leitz for his collaboration in the early stages of this work.

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A Rapid Electrical Method of Separating Carrier-Free Radioactivities

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ELEMENTS with similar chemical properties may be separated by electrical transference methods as shown by the work of Kendall and co-workers.[1–3] We have found a modification of their technique to be of value for rapid separations of carrier-free radioisotopes from other activities and from milligram amounts of non-isotopic carriers.

Our apparatus consists of a stack of filter papers moistened with electrolyte and placed between two platinum electrodes. In a typical separation, a sample of solution containing one or more carrier-free radio-elements, and possibly other stable elements in milligram amounts, was evaporated onto a circular filter paper and placed in the center of the stack which had been previously moistened with a suitable electrolyte. A direct current of 0.04 ampere/cm² for a half hour was sufficient to move ions through about 15 layers of filter paper. By a proper choice of complexing ions and *p*H, the desired activity could be moved to either one of the electrodes or retained at the initial position in the center of the stack. In some mixtures, one activity migrated to one of the electrodes, milligram amounts of non-isotopic elements to the other, while impurity activities remained at the initial position. Recovery of the desired fraction consisted simply of removing filter papers from the appropriate region of the stack. The activity was usually concentrated in less than five adjacent papers.

In each of the separations described below, 0.20 ampere was passed for one half hour through a stack of 30 filter papers, 2.6 cm in diameter.

(1) Separation of carrier-free radio-columbium from manganese dioxide precipitate: A solution of the precipitate in 5 percent oxalic acid was evaporated onto a filter paper and placed in the middle of the stack which had been saturated with 1*m* ammonium oxalate solution. Under these conditions, columbium migrated to the anode region and manganous ions migrated to the cathode.

Another sample of precipitate was dissolved in concentrated hydrochloric acid and was placed in a stack saturated with 3*N* hydrochloric acid. The columbium activity remained on the original papers and the manganous ions migrated to the cathode.

(2) Separation of carrier-free radio-columbium and radio-zirconium from radio-yttrium and rare earth activities: A sample of solution was electrolyzed in a stack saturated with 1*m* ammonium oxalate. Columbium and zirconium were recovered in the anode papers. Yttrium and rare earth activities (Eu, Nd, and Pr) remained on the original paper.

(3) Separation of carrier-free radio-arsenic from milligram amounts of copper hydroxide carrier: The precipitate was dissolved and electrolyzed in 3*N* hydrochloric acid. The arsenic activity remained in original position. Cupric ions migrated to the cathode.

The technique has also been used as a rapid preliminary test in establishing the chemical identity of carrier-free radio-isotopes. For example, an activity which is found to migrate in dilute hydrochloric acid cannot be radio-arsenic.

Other applications of this type are obvious.

We are grateful to Dr. J. G. Hamilton for his interest in this problem.

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† This work was performed under the auspices of the U. S. AEC, contract W-7405-eng-48A-1.
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Selection Rules for Singlet-Triplet Perturbations in Polyatomic Molecules

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May 13, 1949

IN a recent paper[1] Shull has shown that the triplet-singlet emission band of benzene has the vibrational structure of a $^1B_{1u}-{}^1A_{1g}$ transition thus showing that the perturbing singlet state is a $^1B_{1u}$ state. The question of the symmetry of the triplet state required by this observation was not definitely decided, although by analogy with the rule for diatomic molecules that $^3\Sigma^+$ states perturb $^1\Sigma^-$ states, Shull tentatively concluded that

TABLE I. Spin-orbit perturbations in polyatomic molecules.

The + signs mean that all components of the spin-orbit operator connect the states shown. σ means that the principle axis component and π that the perpendicular components connect the states. x, y, and z mean that these particular Cartesian components of the spin-orbit operator connect the states shown.

$C_{\infty v}$	Σ^+	Σ^-	π	Δ
Σ^+	0	σ	π	0
Σ^-	σ	0	π	0
π	π	π	σ	π
Δ	0	0	π	σ

T_d		A_1	A_2	E	F_2	F_1
	0	A_1	A_2	E	F_1	F_2
A_1	A_1	0	0	0	+	0
A_2	A_2	0	0	0	0	+
E	E	0	0	0	+	+
F_2	F_1	+	0	+	+	+
F_1	F_2	0	+	+	+	+

D_6	A_1	A_2	B_1	B_2	E_1	E_2
A_1	0	σ	0	0	π	0
A_2	σ	0	0	0	π	0
B_1	0	0	0	σ	0	π
B_2	0	0	σ	0	0	π
E_1	π	π	0	0	σ	π
E_2	0	0	π	π	π	σ

D_4	A_1	A_2	B_1	B_2	E
A_1	0	σ	0	0	π
A_2	σ	0	0	0	π
B_1	0	0	0	σ	π
B_2	0	0	σ	0	π
E	π	π	π	π	σ

C_{2v}		A_1	A_2	B_1	B_2
	D_2	A_1	B_1	B_2	B_3
A_1	A_1	0	z	y	x
A_2	B_1	z	0	x	y
B_1	B_2	y	x	0	z
B_2	B_3	x	y	z	0

the triplet state must be $^3B_{2u}$. A closer study of the selection rules has verified this conclusion.

The simplest way to derive the selection rules is to consider the group properties of the spin-orbit interaction operator. This is the part of the Hamiltonian principally responsible for mixing singlet and triplet states. For a system of n electrons (n even in our case) and m nuclei, the spin-orbit operator can be written:

$$H'=\sum_i^n A_i(l_{xi}s_{xi}+l_{yi}s_{yi}+l_{zi}s_{zi}),$$

with

$$A_i=\sum_k^m \frac{1}{r^3_{ik}}\frac{V(r_{ik})}{r_{ik}}.$$

In this formula, l_{xi} is the operator for the x component of the orbital angular momentum for electron i and s_{xi} is the operator for the x component of the spin angular momentum for electron i. r_{ik} is the distance of electron i from nucleus k, and $V(r_{ik})$ is the potential at the position of electron i due to nucleus k.

H' may be separated into sums whose orbital and spin factors are separately symmetric or antisymmetric under the operation of electron interchange. One component would be:

$$H_x'=\frac{1}{2n}\sum_{i=1}^n\sum_{j=1}^n (A_il_{xi}+A_jl_{xj})(s_{xi}+s_{xj})$$

$$+\frac{1}{2n}\sum_{i=1}^n\sum_{j=1}^n (A_il_{xi}-A_jl_{xj})(s_{xi}-s_{xj})(i\neq j).$$

The first (symmetric) part splits the degenerate triplet level, and the second (antisymmetric) part mixes singlet and triplet states. We shall be interested in the second part.

Assuming now that we have product type spin-orbit functions, the matrix elements of the spin-orbit operator split up into separate integrals over orbital and spin coordinates. The orbital and spin wave functions are assumed to transform properly under the operations of the symmetry group of the molecule. We will consider only the selection rules for the orbital part of the wave function, at present. Presumably, at least one of the triplet components may be perturbed by a singlet state.

The integral over space coordinates will be non-zero when the product of the representation of the wave functions contains the representation of the significant part of the spin-orbit operator, viz. $A_il_{xi}-A_jl_{xj}$ etc. Since the A_i remain unchanged by symmetry operations, the l_i determine the symmetry properties of the spin-orbit operator. The angular momentum operators have the symmetry properties of rotation operators. Hence with the help of character tables the selection rules may be written down. The rules $g\leftrightarrow g$, $u\leftrightarrow u$, $g\leftrightarrow u$ and $+\leftrightarrow -$ are found directly, and agree with what is known from atomic and diatomic molecular spectra. Analogous to the latter rule in D_{6h} is the rule $B_{1u}\leftrightarrow B_{2u}$ which confirms Shull's tentative conclusion. Selection rules for the more important symmetry groups are given in the tables. The rules for D_{6h} etc., may be derived from those given for D_6 by applying the $g\leftrightarrow g$, $u\leftrightarrow u$ rule.

Many of these same results can be obtained from the correlation between the continuous rotation groups and the point groups, established by Bethe.[2] The method used here seems simpler and more direct.

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The Infra-Red Spectrum and Structure of Diazomethane*

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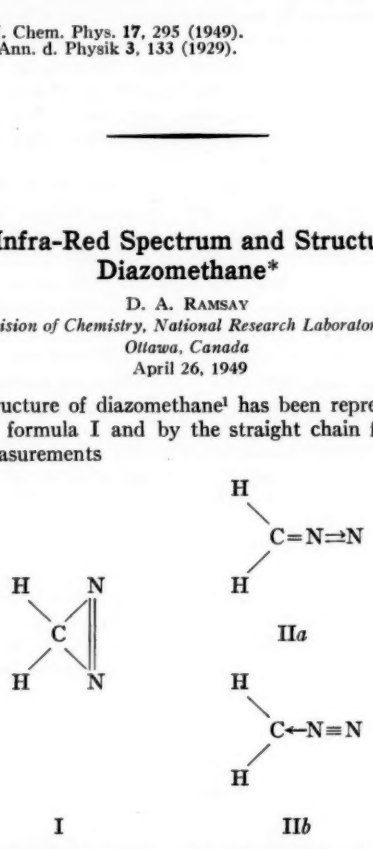
April 26, 1949

THE structure of diazomethane[1] has been represented by a cyclic formula I and by the straight chain formulas II*a* and II*b*. Measurements



I II*a* II*b*

of the ultraviolet absorption spectrum[2] were interpreted in favor of the cyclic structure but electron diffraction investigations[3] subsequently provided strong evidence for a straight chain structure. The low dipole moment[4] of the diazo group however excludes either of the straight chain structures separately, but is consistent with a resonance hybrid of the two structures.

The infra-red spectrum of diazomethane vapor has been measured with a Perkin-Elmer Model 12B infra-red spectrometer and shows a very close similarity to the infra-red spectrum of ketene.[5] Strong "parallel" type bands were observed at 3074, 2103, 1416, and 852 cm^{-1} with PR separations of ~27 cm^{-1} (cf. the ketene bands at 3066, 2153, 1386, and 1120 cm^{-1} with PR spacings of ~25 cm^{-1}). These bands may be assigned to the four totally symmetric vibrations of the straight chain structure. Several perpendicular type bands were resolved and showed the intensity alternation associated with a twofold axis of symmetry.[6] A weak perpendicular type band was observed in the region of 3150 cm^{-1} with a spacing of ~18 cm^{-1} but only three Q branches were free from overlapping by neighboring absorption bands. A complex

band was observed in the region from 1300 to 1000 cm^{-1} with pronounced Q branches at 1176, 1138, and 1099 cm^{-1}, the intensity alternation in this region being very marked. Another weak perpendicular type band was observed in the region from 800 to 650 cm^{-1} with a pronounced intensity alternation but a spacing of only 15 cm^{-1}. A very strong and complex absorption was observed in the region from 650 to 400 cm^{-1} with no apparent regular spacing. This absorption is presumably due to the two skeletal bending vibrations highly perturbed by Coriolis interaction.[7] A more detailed interpretation of the spectrum will be published shortly but sufficient evidence has been presented above to establish conclusively the straight chain structure for the diazomethane molecule.

It is interesting to record that when the absorption spectrum was investigated in a metal cell with KBr windows a change in spectrum was observed on standing. The diazomethane bands disappeared completely during the course of 24 hours and new bands appeared which remained unchanged for several days. Some of these bands were identified as being caused by ethylene, but others could not be explained in this way. In particular two bands were observed at 1180 and 1102 cm^{-1} with well defined PQR structures and PR spacings of approximately 24 cm^{-1}. This spacing is altogether too small for bands of the cyclic monomer but is consistent with the spacing to be expected for the "parallel" bands of the hexacyclic dimer. No change in spectrum was observed, however, when diazomethane was investigated in a glass cell with KBr windows.

The author wishes to express his thanks to Mr. L. C. Leitch for assistance in the preparation of the diazomethane; to Dr. G. Herzberg for valuable discussion and to Dr. R. N. Jones for the use of the spectrometer.

* Published as Contribution No. 1936 from the National Research Laboratories, Ottawa, Canada.

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hydrogen, 0.955; oxygen, 1.02; carbon dioxide, 1.16; stoichiometric methane-air, 1.10. Hence, the energy flow by diffusion in a plane flame may equal or even exceed that caused by thermal conduction, thus yielding zero or negative excess energy; an elementary analysis reveals that the same considerations apply to a spherical flame.

Lewis and von Elbe compare experimental quenching distances with minimum flame radii calculated by their theory from minimum spark energies for ten gas mixtures, obtaining a correlation with 21 percent average deviation and 54 percent maximum deviation. However, this relationship can be treated without recourse to the concept of excess energy, simply by assuming the minimum ignition energy to be proportional to the surface area of the minimum flame sphere, independently of mixture composition and pressure. Minimum flame radii may be correlated with minimum ignition energies in this manner for the above ten mixtures, with 14 percent average deviation and 31 percent maximum deviation. The assumption of invariance with pressure is suggested by consideration of Fig. 3 in an earlier paper[4] by the above authors, which shows minimum ignition energy to be very nearly proportional to the square of quenching distance, and hence to minimum flame surface, over a fivefold pressure range for stoichiometric methane-air mixtures. Lewis and von Elbe's theory does predict the correct order of magnitude for minimum flame radii, but this may be fortuitous.

It is interesting to note that a thermal theory of ignition, such as that suggested by Taylor-Jones, Morgan, and Wheeler[5] and Coward and Meiter[6] would yield the minimum energy to be proportional to the cube rather than the square of the minimum flame radius, as is actually observed. If the thermal theory were modified to include chemical energy liberated in the pre-ignition period, better correlation between theory and experiment might be obtained. However, such a treatment still would be open to the criticism that diffusion is not taken into consideration.

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Spark Ignition of Gas Mixtures

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May 12, 1949

LEWIS and von Elbe[1] have presented a theory of spark ignition based upon the concept of excess energy in a flame front. The present writers wish to point out what appears to be a fundamental weakness in this theory, in that due consideration is not given to the process of diffusion. Lewis and von Elbe evaluate the excess energy integral by considering only thermal energy changes and chemical energy degradation by reaction, while ignoring energy transfer by diffusion.

It is apparent from work published by Jost and von Muffling[2] and by Semenov[3] that energy transfer by interdiffusion of reactants and products is comparable in magnitude with heat conduction. Upon assuming that λ and the product $D\rho$ are independent of temperature, Semenov shows that, for a plane flame, the excess energy vanishes as the dimensionless ratio $D\rho C/\lambda$ approaches unity, where λ is thermal conductivity, D is the diffusion coefficient, ρ is density, and C is specific heat at constant pressure. The values of $D\rho C/\lambda$ at room temperature for some common gases are:

Decrease of an Electrical Discharge by External Radiation

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May 31, 1949

WE have observed the following curious effect.

An H-shaped discharge tube with aluminium electrodes and containing air was used and had side bulbs of P_2O_5 and crushed NaOH. It was run on a.c. and voltage adjusted so that discharge was in its initial stages and consisted of discontinuous bursts of excitation followed by quiescent periods. Light from an incandescent bulb was thrown as a spot of size 5-mm radius on the space just above one of the electrodes. The pressure of air in the discharge tube was 0.7 mm of mercury.

It was found that on external irradiation, the intensity of each burst of discharge as well as the frequency of bursts decreased.

The change was reflected in the decrease of current being fed to the system. The portion of the discharge tube just above the electrode was much more sensitive to external radiation than any other portion of the tube. For optimum voltage setting the discharge could be totally inhibited by the external radiation and appeared as soon as the radiation was removed.

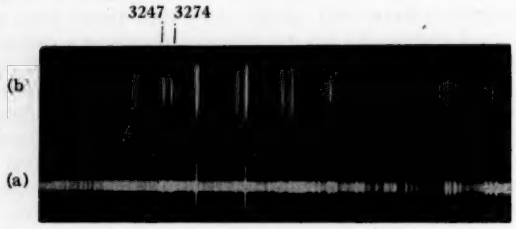

FIG. 1.

Plates (a and b) shows the spectra of the discharge with and without external radiation, for equal exposures. The decrease in intensity on irradiation is clearly noticeable. The superposed spectrum is of copper arc. The incandescent lamp itself gave a continuous spectrum.

* This work was done at the Physical Laboratory, Council of Scientific and Industrial Research, Delhi, India.

Ultrasonic Velocities of Sound in Some Liquid Metals*

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May 31, 1949

THE electronic pulse-circuit technique provides a new and valuable tool for the study of the elastic properties of solids and liquids. The application of this method for investigation of liquids at room temperature is well known.[1] The author has used this same technique for the study of metallic liquids up to 300–350°C under atmospheric pressure. So far, data have been obtained for the more readily available low melting metals—such as sodium, potassium, indium, and tin. Investigations of other low melting liquid metals (cadmium, bismuth, etc.), as well as of certain liquid metallic mixtures, are in progress.

Due to pulse distortions and loss of signal strength (attenuation and/or surface barriers) the precision of the velocity measurements is not better than ±1 percent. However, in view of the absence of data for the elastic properties of the liquid metals in question, the results obtained should still prove valuable. More unfortunate is the fact that this uncertainty makes an accurate determination of temperature coefficients impossible. Such coefficients are given below with due reservation.

In Table I are given the results obtained for the ultrasonic velocities, u, in the mentioned liquid metals at their melting points. Data obtained for mercury at 50° and 150°C are given for comparison.

TABLE I. Sound velocities and temperature coefficients.

Metal	t°C	u (m/sec.)	du/dt (m/sec. deg., approx.)
Na	98	2395±25	−0.3
K	64	1820±20	−0.5
In	156	2215±20	−0.5
Sn	232	2270±20	−0.7
Hg	50	1440±10	−0.7
Hg	150	1370±10	

TABLE II.

Metal	T°K	ρ(g/cm³)	$\alpha\times10^{-4}$	C_p	$k_S\times10^6$(bar^{-1})	C_p/C_v	$k_T\times10^6$ (bar^{-1})
Na	371	0.930	2.8	7.5	18.7 ±0.4	1.12	21.0
K	337	0.835	2.9	7.7	36.2 ±0.8	1.11	40.3
In	429	7.0	1.2	7.0	2.9 ±0.1	1.12	3.2
Sn	505	6.99	1.0	6.6	2.79±0.05	1.11	3.1
Hg	323	13.47	1.82	6.6	3.58±0.05	1.16	4.1
Hg	423	13.23	1.82	6.6	4.03±0.05	1.19	4.8

From these data the adiabatic and isothermal compressibilities k_S and k_T at the same temperatures have been calculated and are given in Table II. Data for the densities, ρ, coefficients of thermal expansion, α, and specific heats, C_p, have been taken from Landolt-Börnstein and International Critical Tables. In the absence of data for the density and coefficient of thermal expansion for liquid indium, these have been estimated to be 7.0 g/cm³ and 1.2×10^{-4} deg.$^{-1}$, respectively.

Mercury is the only metal for which previous data exist under similar temperature conditions. Carnazzi[2] gives for mercury $k_T=3.9\times10^{-6}$ atmos.$^{-1}$ at 52.8°C and 4.4×10^{-6} at 150.3°C. In view of the discrepancy between Carnazzi's values and the results of more recent investigations at room temperature (Carnazzi: $k_T=3.8\times10^{-6}$, while the accepted value is 4.0×10^{-6} atmos.$^{-1}$), the disagreement with the present investigation should not be disturbing. An interesting feature of the data above is the constant value of C_p/C_v at the melting points of the four metals, Na, K, In, Sn. Even if due allowance is made for the uncertainties associated with the accepted values for densities, expansion coefficients, and specific heats, this agreement is remarkable, and may have theoretical significance.

I am indebted to Dr. David Lazarus for invaluable technical help.

* This work has been supported in part by the ONR under Contract N-6ori-20-XX with the University of Chicago.

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Extension of Fowler's Treatment of Surface Tension to Physical Adsorption

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May 5, 1949

THE free volume model of a liquid can be applied to a liquid-like adsorbate[1] (of, say, three or more layers). We give here an analogous extension of Fowler's[2] treatment of surface tension. We are investigating both of these approximate approaches to this problem in more detail.

Consider a plane slab of liquid of area $\mathfrak{A}$, thickness h, and density $\rho(\rho=N/V)$. In the present approximation we assume that ρ and the usual molecular distribution function $g(r)$ are the same in the slab as in the bulk liquid. Let A be the Helmholtz free energy of the slab in its equilibrium position in the presence of adsorbent. Let A_0 refer to the slab in the bulk liquid. $A-A_0$ is then the reversible isothermal work W done on the system in (1) breaking a column of liquid of area $\mathfrak{A}$ at $z=0$ and removing the part $z<0(W_1)$, (2) breaking the remaining liquid at $z=h$ and removing the part $z>h(W_2)$, (3) bringing the slab $0<z<h$ up to its equilibrium position next to the adsorbent (W_3), and (4) rejoining the parts $z<0$ and $z>h(W_4)$. Since $W_1+W_4=0$, $A-A_0=W_2+W_3$. The adsorption isotherm is then

$$kT\ln p/p_0=\partial(W_2+W_3)/\partial N. \qquad (1)$$

Let $u(r)$ be the interaction energy between two liquid molecules, and $F(r)=-du(r)dr$. Then, on making straightforward modifica-

tions of Fowler's argument, one finds

$$-W_2=\pi\rho^2\mathfrak{A}\Big(\tfrac{1}{4}\int_0^h r^4g(r)F(r)dr+\frac{2h}{3}\int_h^\infty r^3g(r)F(r)dr$$
$$-\frac{h^2}{2}\int_h^\infty r^2g(r)F(r)dr+\frac{h^4}{12}\int_h^\infty g(r)F(r)dr\Big), \quad (2)$$

and

$$\partial(-W_2)/\partial h=\pi\rho^2\mathfrak{A}\Big(\tfrac{2}{3}\int_h^\infty r^3g(r)F(r)dr$$
$$-h\int_h^\infty r^2g(r)F(r)dr+\frac{h^3}{3}\int_h^\infty g(r)F(r)dr\Big). \quad (3)$$

The type of detailed computation of W_2 used will depend on the nature of the adsorbent. For simplicity, we confine ourselves here to the following very approximate treatment: assume the adsorbent is structureless and that it does not perturb $g(r)$. Let the interaction energy between an adsorbent molecule and a liquid molecule be

$$u_1=\epsilon_1(r_1/r)^{12}-2\epsilon_1(r_1/r)^6. \quad (4)$$

Then the interaction energy between the entire adsorbent (density ρ_1) and a liquid molecule at a distance z from the plane adsorbent surface is[3]

$$\varphi=(\alpha/z)^9-(\beta/z^3)$$
$$\alpha=\epsilon_1r_1^{12}\pi\rho_1/45 \quad (5)$$
$$\beta=\epsilon_1r_1^6\pi\rho_1/3,$$

and the force is $-d\varphi/dz$. On integration, one finds the total interaction energy Φ between the liquid slab and the adsorbent (nearest edge of slab at distance z from adsorbent), and the corresponding total force f. Setting $d\Phi/dz=0$ gives the equilibrium value of z, $z_0(h)$:

$$\alpha[(z_0+h)^{-9}-z_0^{-9}]=\beta[(z_0+h)^{-3}-z_0^{-3}]. \quad (6)$$

Then

$$W_3=\int_{z_0}^\infty f dz$$
$$=\mathfrak{A}\rho\{(\alpha/8)[z_0^{-8}-(z_0+h)^{-8}]-(\beta/2)[z_0^{-2}-(z_0+h)^{-2}]\}, \quad (7)$$

and

$$dW_3/dh=\mathfrak{A}\rho[\alpha(z_0+h)^{-9}-\beta(z_0+h)^{-3}]. \quad (8)$$

Substitution of Eqs. (3) and (8) into Eq. (1), using $N=\mathfrak{A}\rho h$, gives the adsorption isotherm. If we use

$$u(r)=\epsilon(r^*/r)^{12}-2\epsilon(r^*/r)^6 \quad (9)$$

the isotherm reduces, for large $\Gamma=N/\mathfrak{A}$, to

$$\ln p/p_0=(\delta-\delta_1)/\Gamma^3, \quad (10)$$
$$\delta=\pi\rho^4\epsilon r^{*6}/3kT, \quad (11)$$
$$\delta_1=\pi\rho^3\rho_1\epsilon_1r_1^6/3kT. \quad (12)$$

Equation (10) is identical with Eq. (9) of reference 1, so we shall not discuss it further here.

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Raman and Infra-Red Spectra of Oxalyl Chloride

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May 11, 1949

THE infra-red spectrum in the region 400–10000 cm^{-1} and the displacements, semiquantitative relative intensities, and depolarization factors of the Raman lines have been obtained for liquid oxalyl chloride (ClOC–COCl) at room temperature. The depolarization factors were obtained by a previously described method[1] and the relative intensities were obtained with the aid of a Gaertner microdensitometer.[2] The infra-red absorption data were secured from records obtained with a Beckman IR-2 spectrophotometer with KBr optics. With a few exceptions, the present Raman data are in reasonably good agreement with the previous Raman data. So far as the authors have been able to determine, no previous infra-red data have been reported. The results are given in Table I.

TABLE I. Raman and infra-red spectral data for liquid oxalyl chloride (ClOC–COCl).*

Raman			Infra-red	
$\Delta\nu$	I	ρ	ν	I_e
193	5	0.88		
261, 279	33	0.37		
354	3	(0.96)		
443	21	0.51		
465	28	0.48		
483	30	0.50	488	*S*
522	7	*P*		
533	12	*P*	532	*S*
			594	*S*
620	100	0.17		
709	1	—		
			752	*VVS***
802	*VW*	—		
			942	*S*
			1058	*VVS*
1081	5	0.32		
			1310	*VS*
			1388	*S*
1416	*VW*	—		
			1754	*VVS*
1781	57	0.79		
			1826	*VVS*
			2510	*S*
			2830	*VS*
			3740	*VS*
			5140	*W*

* $\Delta\nu$ is the Raman displacement in cm^{-1}, I is the relative intensity on the basis of 100 for the strongest Raman line, ρ is the depolarization factor, ν is the wave number corresponding to the maximum absorption in the infra-red band, I_e is the estimated intensity of the infra-red bands (*VVS* = very, very strong; *VS* = very strong; *S* = strong; *W* = weak; *VW* = very weak); data in regard to which there is some uncertainty are enclosed in parentheses; and *P* indicates lines for which quantitative values of ρ could not be determined but which appear to be polarized.
** Middle of a very broad band.

An examination of the Raman and infra-red data indicates that there are only two coincident frequencies. Since in view of the large number of frequencies these two could well be chance coincidences, the rule of mutual exclusion may apply. If this is the case, the oxalyl chloride molecule has a center of symmetry and the structure would be that corresponding to the *trans*- or C_{2h} form. The values obtained for the depolarization factors and the absence of a second line near 1781 cm^{-1} in the Raman spectrum represents additional evidence for the *trans*-form. This evidence is in partial agreement with the conclusion reached by Martin and Partington[3] on the basis of dipole moment and molar refractivity measurements, namely, that the small dipole moment of 0.92 Debye unit could be explained by either free rotation or oscillation about the stable *trans*-position.

A normal coordinate treatment (*FG* matrix method) is being carried out for the *trans*- model in order to determine whether a satisfactory assignment of the observed frequencies can be made on the basis of this model. Further experimental details and the results of the normal coordinate treatment will be reported later.

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A Variational Iteration Method for Solving Secular Equations

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May 24, 1949

WE shall describe a simple and rapidly convergent method for the solution of homogeneous linear equations, which is based on the well-known stationary property of eigenvalues but has apparently escaped notice so far.

To find the eigenvalues, E, and amplitudes, a_i, of the system of equations,

$$\sum_{j=1}^{n} H_{ij}a_j = Ea_i \quad i=1, 2, \cdots n, \tag{1}$$
$$(H_{ij}=H_{ji})$$

one adopts the following procedure:

Step 1: Obtain by some means (not provided by this method) a value, $E^{(0)}$, as a first rough approximation to one of the eigenvalues. *Step 2:* Omit one of the equations, the kth say, from the system (1), preferably that whose diagonal element lies closest to $E^{(0)}$. (This choice speeds convergence.) Set $a_k=1$ and solve the remaining $(n-1)$ equations for the a_i, using the approximate $E^{(0)}$ in place of E. The resulting amplitudes, $a_i^{(0)}$, satisfy the equations

$$\sum_{j=1}^{n} H_{ij}a_j^{(0)} = E^{(0)}a_i. \quad i=1, \cdots k-1, k+1, \cdots n. \tag{2}$$

Compute $\sum_{i=1}^{n} (a_i^{(0)})^2$. *Step 3:* Use the $a_i^{(0)}$ to determine an intermediate estimate for E, $E^{(\frac{1}{2})}$, from the kth equation:

$$\sum_{j=1}^{n} H_{kj}a_j^{(0)} = E^{(\frac{1}{2})}. \tag{3}$$

Step 4: An improved variational estimate of E, $E^{(1)}$, is obtained from the stationary expression

$$E^{(1)} = \sum_{i=1}^{n}\sum_{j=1}^{n} a_i^{(0)}H_{ij}a_j^{(0)} / \sum_{i=1}^{n} (a_i^{(0)})^2$$
$$= E^{(0)} + (E^{(\frac{1}{2})} - E^{(0)}) / \sum_{i=1}^{n} (a_i^{(0)})^2. \tag{4}$$

Here Eqs. (2) and (3) have been used to simplify. *Step 5:* If $E^{(1)}$ is not sufficiently accurate, return to step 2 and repeat the entire procedure using $E^{(1)}$ in place of $E^{(0)}$ to obtain $a_i^{(1)}$, $E^{(\frac{1}{2})}$ and hence $E^{(2)}$, etc.

This procedure converges to *any* eigenvalue of (1), if only $E^{(0)}$ is chosen sufficiently closer to it than to the nearest other eigenvalue; i.e., if

$$\delta E^{(0)}/D \ll \tfrac{1}{2}, \tag{5}$$

where δ denotes the difference from the correct eigenvalue to be found and D is the level spacing. The following qualitative argument will make this clear: If $E^{(0)}$ has an error of the first order, so will the $a_i^{(0)}$ computed in step 2. When these are substituted into the stationary expression (4), the resulting $E^{(1)}$ has an error of the second order. Hence the next set, $a_i^{(1)}$ have a second-order error and $E^{(2)}$ has an error of the fourth order, etc. A more careful analysis shows that

$$\delta E^{(n+1)}/D = K_n(\delta E^{(n)}/D)^2, \tag{6}$$

where K_n is in general of the order 1. However, when H_{ij} is nearly diagonal, K_n is of the order $\Delta E/D$, where ΔE is the shift of the eigenvalue caused by the small off-diagonal elements, and thus the convergence is even more rapid.

This method has been used in combination with the technique of James and Coolidge[1] in which $E^{(n+\frac{1}{2})}$ and the $a_i^{(n)}$ are directly obtained. In many practical cases a single iteration is sufficient. Thus Mr. R. Clapp, working with an 11-dimensional determinant, with $D\approx 2$, and starting with $E^{(0)}=0.8800$, obtained $E^{(1)}=0.9088$, with an error of less than 0.0001.

Mr. D. Robinson is using the method here described in conjunction with an electric network technique[2] for a study of molecular vibration spectra. Here $E^{(n+\frac{1}{2})}$ and $a_i^{(n)}$ are directly read off the apparatus and hence $E^{(n+1)}$ is easily obtained.

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[1] H. M. James and A. S. Coolidge, J. Chem. Phys. **1**, 825 (1933).
[2] A. A. Frost and M. Tamres, J. Chem. Phys. **15**, 383 (1947).